French Standard NF T 45-007:   Primary materials for the rubber
    industry: Precipitated hydrated silica*   [Norme Français NF
    T 45-007:   Matières premières pour l'industrie du
    caoutchouc: Silices hydratées précipitées]

*   November, 1987

FRENCH STANDARD

NF T 45-007

November 1987

PRIMARY MATERIALS FOR THE RUBBER INDUSTRY
PRECIPITATED HYDRATED SILICA

French standard ratified by decision of the General Director of
AFNOR October 20, 1987, to take effect November 20, 1987.
Replaces the ratified standard of May, 1972, with the same index.

Correspondence: On the date of publication, the present standard
is not equivalent to standards ISO 5794 part 1 of 1984 and part 2
of 1982 (see preface).

Analysis: The present standard describes the characteristics and
corresponding test methods of precipitated hydrated silicas for
use in rubber mixtures. The precipitated hydrated silicas
consist of amorphous particles obtained by precipitation by the
action of an acid with an aqueous alkaline silicate. The
precipitated hydrated silicas constitute a reinforcing load for
rubber.
      The level of reinforcement depends to a large extent on the
specific surface area.

Descriptive terms: Thesaurus International Technique
[International Technical Thesaurus]: elastomer industry, rubber,

primary material, silica, specific surface area, characteristic, test methods.

Modifications: With respect to the preceding edition, which specified a single class of precipitated hydrated silica, the present standard describes the characteristics of four classes based on the specific surface areas.

Corrections:

[footer, p. 1:]
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[header, p. 2]
Primary materials for the rubber industry   NF T 45-007
Precipitated hydrated silica   November 1987

Preface
     On the date of publication, there exists the international standard ISO 5794 (parts 1 and 2) to which the present standard is not equivalent: the differences relate to:
     – the classification of silica according to area per unit weight;

- the determination of the specific surface area;

- the characteristics (value or nature).

The value of certain characteristics is different from those of the ISO specifications with regard to:

- the silica content of the dry sample (calcined at 1,000°C);

- the metallic sieve residue;

- the copper, manganese and iron contents.

Other characteristics are presented because of they are of value to the user of precipitated silica in the rubber industry; they are:

- the silica content of the sample in the state it is in;

- the soluble copper content;

- the loss on combustion based on the product in the state it is in;

- the conductivity of a suspension of silica in water;

- the total and external specific surface area.

  - the test techniques relating to:

- pH;

- conductivity of a suspension of silica in water.

The technique of the tests on mixtures is identical to that of the international standard ISO 5794/2.

Contents

1 PURPOSE AND FIELD OF APPLICATION

The purpose of the present standard is to set the characteristics of precipitated hydrated silicas in powder form or in another presentation (granules, microbeads) which are intended for the rubber industry and the corresponding test methods. It does not apply to natural silicas or to the special grades of silica that have undergone a surface treatment.

The silicas to which the standard relates are included in one of the following specific surface area classes (paragraph 5.11):

Class	Specific surface area, m^2/g
A	231-290
B	161-230
C	101-160
D	≤ 100

2 REFERENCES

NF B 35-001   Glassware and laboratory equipment and associated apparatuses - Beakers.

NF B 35-306   Glassware and laboratory equipment and associated apparatuses - Graduated pipettes.

NF B 35-307   Glassware and laboratory equipment and associated apparatuses - Volumetric flasks with one line.

NF B 35-504   Precision thermometers, with a protected scale, long type.

NF T 01-012   pH-metry - Standard solutions for calibration of a pH meter.

NF T 43-004   Rubber - Determination of the scorch time and the vulcanization index of mixtures of unvulcanized rubber, using the shear viscometer.

NF T 43-005   Rubber - Determination of the viscometric index of unvulcanized rubber, using the shear viscometer.

NF T 43-006   Rubber and similar elastomers - Preparation and vulcanization of reference mixtures.

NF T 45-002   Primary materials for the rubber industry - Zinc oxide.

NF T 45-003   Primary materials for the rubber industry - Sulfur.

NF T 45-004   Primary materials for the rubber industry - Technical stearic acid.

NF T 46-002   Vulcanized or thermoplastic rubber - Tensile test.

NF T 46-003   Rubber and similar elastomers - International hardness test for vulcanized rubbers (30-94 D.I.D.C. [expansion unknown]).

NF T 46-007   Rubber - Determination of the tear strength of vulcanized rubber (notched or unnotched angular test pieces, and crescent-shaped test pieces).

X 06-065 Introduction to the use of statistical tests - Comparison of two samples.

NF X 11-621   Determination of the area per unit of weight (specific surface area) of powders by adsorption of gas - BET method - Volumetric measurement by nitrogen adsorption at low temperature.

X 11-622 Determination of the area per unit of weight
(specific surface area) of powders by adsorption of gas -
Variants of the basic method.

3   DEFINITION

The hydrated silicas generally consist of amorphous
particles obtained by precipitation with an acid from a soluble
silicate.

CHARACTERISTICS

Designation	Characteristics	Test method
Appearance	Fine white powder, white granules, white microbeads.	
Color	Roughly identical to that of a sample certified by agreement by the contracting parties.	Direct visual comparison with the specimen. In case of dispute, proceed with a quantitative determination of whiteness (apparatus of the Elrepho or Gardner type).
45 μm metallic sieve residue	$\leq 0.1\%$ by appearance.	Paragraph 5.1
Volatile material content at 105°C	Between 3 and 8%.	Paragraph 5.2
Loss on combustion	$\leq 7\%$ based on dry product. $\leq 12\%$ based on product in the state it is in.	Paragraph 5.3
SiO_2 content	$\geq 90\%$ based on dry product. $\geq 83\%$ based on the product in the state it is in.	Paragraph 5.4
pH	Between 5 and 8.	Paragraph 5.5
Soluble copper content	≤ 2 mg/kg	Paragraph 5.6
T tal copper content	≤ 30 mg/kg	Paragraph 5.7
Total manganese content	≤ 50 mg/kg	Paragraph 5.8
Total iron content	≤ 500 mg/kg	Paragraph 5.9
Conductivity of a suspension of silica in water	$\leq 3,600$ μS at 20°C	Paragraph 5.10
Specific surface area (nitrogen adsorption)	Set by agreement between the contracting parties.	Paragraph 5.11
External specific surface area (CTAB adsorption)	Set by agreement between the contracting parties.	Paragraph 5.12

Tests on mixtures
 	
 a) In th unvulcanized state
    1 - viscometric index
    2 - scorch time and vulcanization index
 	
 b) In the vulcanized state:
    1 - break strength
    2 - elongation at break
    3 - modulus at 500% elongati n
    4 - international hardness
    5 - tearing.
	Set by agreement between the contracting parties.	Paragraph 5.13
		
		 NF T 43-005
		
		 NF T 43-004
		
		 NF T 46-002
		 NF T 46-002
		 NF T 46-002
		 NF T 46-003
		 NF T 46-007

5   TEST METHODS

5.1 Determination of the sieve residue

5.1.1   Equipment

Sieve, diameter 100 to 200 mm, with edges 50 mm high, and 45-μm openings.

Glass rod, with a rubber endpiece with a hardness of 50 according to NF T 46-003.

1-L beaker.

Balance accurate to the nearest 0.1 g.

Filtering crucible, with a sintered glass plate, porosity P 40 (pore diameter 16 to 40 μm).

Water supply, at a pressure equivalent to a water height of 1 m.

Sprinkling rose according to Figure 1.

Dimensions en millimètres ①

② 25 trous sur
la ligne médiane

③ 25 lignes équidistantes de trous de diamètre 0,4 à 0,5,
les trous étant décalés dans les lignes successives.

④ Les trous près du bord doivent avoir leurs centres à au
moins 1 mm du bord.

Φ5

Tube

Φ50

⑤ Plaque de tamis en métal convenable

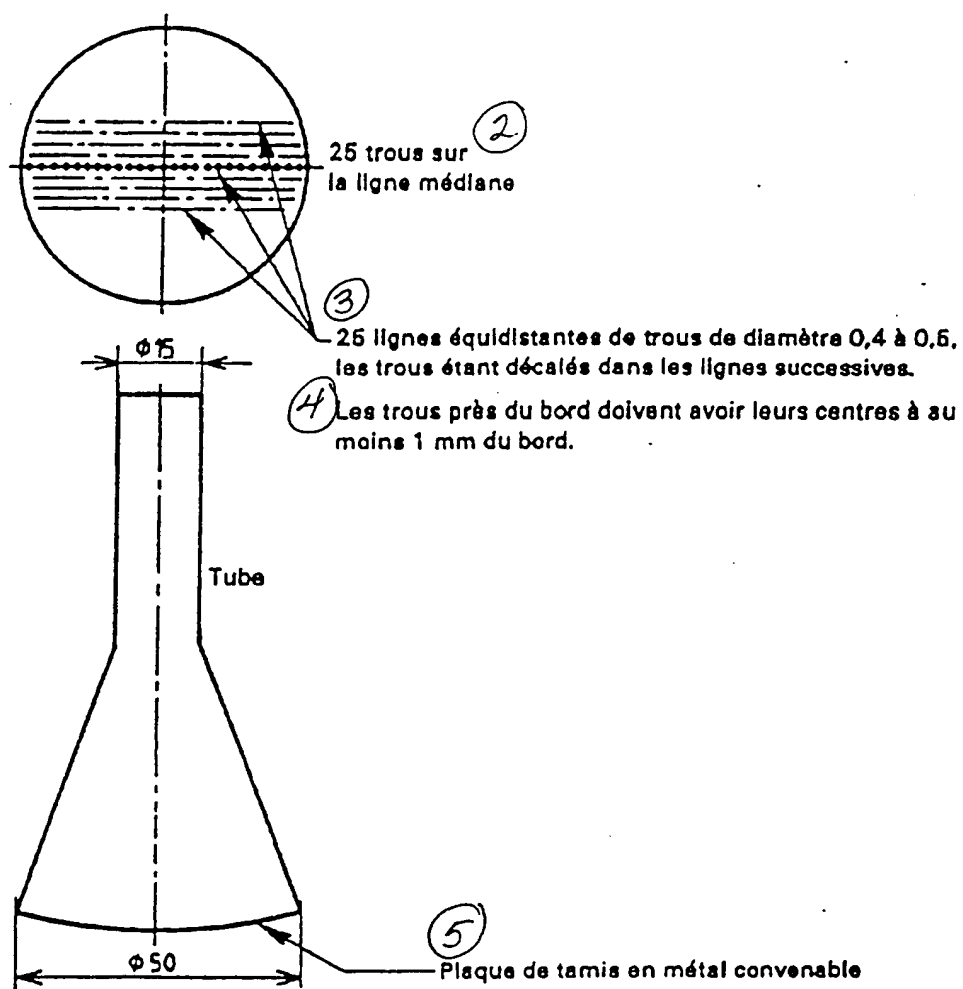Figure 1

Key: 1   Dimensions in millimeters
    2   25 holes on the middle line
    3   25 equidistant lines of holes, diameter 0.4 to 0.5; the holes are offset in successive lines.
    4.   The holes near the edge must have their centers at least 1 mm from the edge.
    5   Sieve plate made of a suitable metal

5.1.2   Procedure

In a beaker, weigh to the nearest 0.1 g between 50 and 500 g (see note) of the sample to be examined. Disperse the silica in a sufficient quantity of water (usually on the order of 500 to 600 mL) using the glass rod with the rubber endpiece only to facilitate dispersion, and pour the dispersion through the appropriate sieve. Transfer the sieve residue to the beaker, and repeat the dispersing operation (without adding dispersant), using a similar quantity of water; pour through the sieve as in the preceding. Repeat this operation, and wash the residue remaining in the beaker with water using the glass rod if necessary.

Wash the residue on the sieve using the sprinkling rose connected to the water supply at constant height until the washing water is clear.

Wash the residue in the previously weighed sintered glass plate crucible, and dry it at 105°C ± 2°C. Cool in a desiccator, and weigh to the nearest 0.1 mg. Repeat the heating, cooling and weighing until a constant weight is obtained.

Note: The weight of the chosen load material must be such that the anticipated sieve residue is as close as possible to approximately 0.2 g.

5.1.3   Expression of the results

The sieve residue, in weight percent, is given by the formula:

$$100\ m_1/m_0$$

in which:

m_0 is the weight in grams of the test sample;

m_1 is the weight in grams of the residue.

5.2 Determination of the content of volatile materials

5.2.1   Equipment

Weighing vessel, low form, with a large neck, with a ground glass stopper.

Oven that can be maintained at 105°C ± 2°C.

Balance, accurate to the nearest 0.001 g or better.

Desiccator, lined with an effective dehydration agent.

5.2.2   Procedure

Carry out two determinations.

- Test sample

Heat the weighing vessel, with the stopper removed, in the oven at 105°C ± 2°C for 2 h. Allow to cool in the desiccator, stopper, and weigh to the nearest 0.001 g.

Spread 10 g ± 1 g of sample in a uniform layer on the bottom of the weighing vessel, stopper, and weigh to the nearest 0.001 g.

- Determination

Heat the weighing vessel and its contents, with the stopper removed, in the oven at 105°C ± 2°C for at least 1 h. Allow to cool in the desiccator, stopper, and weigh to the nearest 1 mg. Repeat the heating for at least 1 h, allow to cool in the desiccator, stopper, and weigh again to the nearest 1 mg. Repeat these operations until two successive weighing operations do not differ by more than 5 mg. Note the lowest weight.

If the results of two determinations differ by more than 10% of the higher value, repeat the entire procedure.

5.2.3   Expression of the results

The content of volatile materials at 105°C, expressed in weight percent, is given by the formula:

$$100(m_0 - m_1)/m_0$$

in which:

m_0 is the weight in grams of the test sample;

m_1 is the weight in grams of the residue.

Calculate the average of two determinations if they do not differ by more than 10% of the higher value, and note the result to the nearest 0.1%. Indicate the results between 0 and 0.1% as "less than 0.1%."

5.3 Determination of the loss on combustion

5.3.1   Based on dry product

5.3.1.1   Equipment
Not very deep porcelain or platinum crucible.
Desiccator.
Balance accurate to the nearest 1 mg or better.
Muffle furnace that can reach a temperature of 1,000°C ± 25°C.

5.3.1.2   Procedure
Weigh to the nearest 0.001 g in the weighed porcelain or platinum crucible approximately 2 g of previously dried silica as described in paragraph 5.2.2.
Introduce the crucible and its contents into a cold furnace, whose temperature is gradually raised up to 1,000°C ± 25°C (over approximately 2 h) and is maintained there until a constant weight is obtained in an oxidizing atmosphere. Then, allow the crucible to cool down to approximately 300°C in the furnace, and then place it in the desiccator until it is completely cooled. Then, proceed to weigh it to the nearest 0.001 g.

5.3.1.3   Expression of the results
The loss on combustion, expressed in weight percent, is given by the formula:
$$100(m_0 - m_2)/m_0$$

in which:

m_0 is the weight in grams of the test sample;

m_2 is the weight in grams of the test sample after calcining.

5.3.2   Based on the product in the state it is in

One proceeds as in the case of the dry product, but one does the determination on a sample of product removed from the original package without doing the preliminary drying at 105°C.

5.4   Determination of the SiO_2 content

5.4.1   Principle

Hydrofluoric acid in the presence of sulfuric acid quantitatively transforms silica into gaseous SiF_4. The weight loss of the sample thus treated allows one to assess its SiO_2 content.

5.4.2   Based on dry product

5.4.2.1   Reagents

Sulfuric acid, 50% solution (V/V).

Hydrofluoric acid, 40% (weight/weight).

5.4.2.2   Equipment

Platinum crucible.

Muffle furnace.

Desiccator.

Balance accurate to the nearest 0.001 g.

5.4.2.3   Procedure

Place the dried silica, obtained as described in paragraph
5.2.2, in the platinum crucible, and add 1 mL of sulfuric acid.
Heat the crucible slowly until the fumes stop, and then continue
to heat to 900°C for 15 min in the muffle furnace. Remove the
crucible from the furnace, cool in a desiccator, and weigh to the
nearest 0.001 g (m_3).

Add 15 mL of hydrofluoric acid and 1 mL of sulfuric acid to
the residue in the platinum crucible, and evaporate until
obtaining a syrup, taking care to avoid losses due to splashing
of material. Cool the container and wash the walls with water.
Then, add 10 mL of hydrofluoric acid, and evaporate to dryness.
Heat the residue on a hot plate until no more white fumes are
produced; then calcine in the muffle furnace at 900°C for 15 min.

Remove from the furnace, cool in a desiccator, and weigh
(m_4).

5.4.2.4   Expression of the results

The silica content, expressed in weight percent, is given by
the formula:

$$(m_3 - m_4)/m_1 \times 100$$

in which:
m_1 is the weight in grams of silica dried at 105°C obtained in
5.2;
m_3 is the weight in grams after calcination with sulfuric acid;
m_4 is the weight in grams after calcination with hydrofluoric
acid.

5.4.3   Based on the product in the state it is in

One proceeds as in the case of the dried product, but one does the determination on a sample of the product removed from the original package without preliminary drying.

The silica content of the product in the state it is in, expressed in weight percent, is given by the formula:

$$(m_3 - m_4)/m_0 \times 100$$

in which:

m_3 and m_4 correspond to the respective definitions given in 5.4.2.4;

m_0 is the weight in grams of the test sample.

5.5   Determination of the pH

5.5.1   Equipment

250-mL beaker, tall form, made of borosilicate glass.

100-mL graduated test tube.

Balance accurate to the nearest 0.001 g.

Instrument for measuring the pH, capable of giving a measurement to the nearest 0.1 unit, calibrated at the test temperature with respect to standard solutions with known pH. This measuring instrument can be, for example, a suitable pH meter with glass electrodes.

Magnetic stirrer.

5.5.2   Reagents

Freshly distilled water, boiled before it is used in order to eliminate the carbon dioxide, or water of equivalent purity prepared in another manner.

Standard solutions suitable for calibrating the pH-measuring instrument (NF T 01-012).

5.5.3   Procedure

Weigh 5 g of silica to the nearest 0.02 g and then transfer it to the 250-mL beaker.

Add 100 mL of distilled water (5.5.2) previously boiled for 10 min and cooled in a stoppered bottle. Stir the dispersion of silica in the water for 7 min using the magnetic stirrer. Bring to a boil. Cool to 20°C. Possibly compensate for the evaporation by adding distilled water. Measure the pH after calibration of the measuring instrument. The measurement of the pH of the suspension is done at 20°C ± 1°C with continual stirring during the measuring.

5.6 Determination of the soluble copper content

5.6.1   Principle

Corrosion of the test sample by hydrochloric acid, then spectrometric or colorimetric determination of the amount of copper in the diethyldithiocarbamate form.

5.6.2   Equipment

Buchner funnel, 90 mm in diameter.

100-mL, 250-mL, and 1,000-mL volumetric flasks, NF B 35-307.

5-mL and 10-mL pipettes, NF B 35-306.

100-mL and 250-mL glass beakers, NF B 35-001.

500-mL spherical separatory funnel.

Slow-filtering ash-free filter paper.

Spectrometer (wavelength: approximately 400 nm) or 50-mL Nessler tubes with practically the same coloring and the same wall thickness.

Balance accurate to the nearest 0.0001 g.

Liquid jet vacuum pump with appropriate accessories.

5.6.3   Reagents
During the analysis:

5.6.3.1   Hydrochloric acid (ρ_{20} = 1.19 g/mL).

5.6.3.2   Water distilled in a glass or stainless steel apparatus in order to avoid traces of copper.

5.6.3.3   Citric acid - 1,000 g/L solution.

5.6.3.4   Ammonia - concentrated solution (ρ_{20} = 0.90 g/mL).

5.6.3.5   Zinc diethyldithiocarbamate - solution in chloroform prepared in the following way:

Dissolve 2 g of zinc sulfate heptahydrate in 100 mL of distilled water. Add 1 g of sodium diethyldithiocarbamate weighed to the nearest 0.001 g. Introduce the suspension into the 500-mL spherical separatory funnel, add 100 mL of chloroform,

and stir vigorously; collect the chloroform phase, and bring to the volume of a 1,000-mL volumetric flask using chloroform.

This solution must be kept in a brown bottle and must be used within 8 days maximum.

5.6.3.6   Copper - Standard solutions prepared as follows:

Weigh to the nearest 0.001 g 0.393 g of copper sulfate pentahydrate in a 250-mL beaker. Dissolve in 100 mL of distilled water, and then add 5 mL of concentrated sulfuric acid with a density at 20°C of 1.83/mL. Fill to the volume of a 1,000-mL volumetric flask with distilled water.

Solution A

Remove 100 mL of this solution using a volumetric flask; transfer to a 1,000-mL volumetric flask, and fill to the volume with distilled water.

1 mL of this solution contains 0.00001 g of copper.

Solution B

Remove 100 mL of solution A and dilute to 1,000 mL as in the above.

1 mL of this solution contains 0.000001 g of copper.

5.6.4   Procedure

Weigh 10 g of silica, dried as indicated in paragraph 5.2.2, to the nearest 0.001 g. Add 30 mL of hydrochloric acid and 30 mL of distilled water. Bring to a slow boil for 15 min in order to avoid splashing material; then allow to cool, quantitatively filter using a Buchner funnel lined with two slow filters, and

transfer the filtrate to a 250-mL volumetric flask. Add 10 mL of citric acid in order to complex the iron, and fill to 250 mL with distilled water.

Transfer quantitatively into the spherical separatory funnel, and add ammonia until obtaining a pH of at least 9, while stirring continually (30 mL is generally sufficient).

Extract the copper using the 3 fractions of 10 mL each of zinc diethyldithiocarbamate in solution in chloroform while stirring vigorously; if the third fraction is still yellow in color, proceed with a fourth extraction. Combine the solutions in chloroform in a Nessler tube. Fill to 50 mL with chloroform, and proceed to measure the absorbance, or compare the color obtained with that of the solutions prepared in the following manner.

5.6.4.1   Preparation of the color scale

If a calibration curve done with the spectrometer is not available, place in a series of 250-mL volumetric flasks: 2.5 mL, 5 mL, 10 mL, 15 mL, and 25 mL of one of the standard copper solutions A or B, depending on the concentration of the copper in the silica. Add to each flask 10 mL of citric acid, and fill to 250 mL with distilled water.

Quantitatively transfer into spherical separatory funnels, add ammonia with continuous stirring until obtaining a pH of 9. Extract the copper using 3 or 4 fractions of 10 mL each of zinc diethyldithiocarbamate in solution in chloroform, while stirring vigorously. Combine the solutions in chloroform in a Nessler tube. Fill to 50 mL using chloroform.

5.6.4.2   Determination

a) Measure the absorbance at a wavelength in the vicinity of 440 nm.

b) If no spectrometer is available, compare the coloring of the test solution with that of the series of solutions constituting the color scale, (solution A or solution B), proceeding in the following way:

- if X is the number of milliliters of the copper solution which gives a coloring roughly equivalent to that of the tested solution, supplement the color scale in order to improve the accuracy of the measurement by preparing new solutions of copper diethyldithiocarbamate using:

(X - 2) mL, (X - 1) mL, X mL, (X + 1) mL, (X + 2) mL of standard solution (5.6.3.6).

Compare the coloring of the tested solution with the new series of colors produced;

- if the coloring given by the solution to be analyzed is more intense than that obtained with 25 mL of standard solution A, proceed with a smaller portion of the solution to be analyzed, for example: 25 mL or even 12.5 mL if the coloring is very intense, instead of the 50 mL provided for above in 5.6.4.1.   It will then be necessary to multiply the final result by 2 or by 4, respectively.

5.6.5   Blank test.

a) If a spectrometer is used, the adjustment must be done at the time of the determination with the test solution containing all the reagents, with the exception of the silica.

b) If working with the color scale, determine the amount of copper contained in the reagents by comparison with the standard series produced at the time of the determination.

5.6.6   Expression of the results

a) If the measurement was made with a spectrometer, the copper content, expressed in weight percent, is given by the formula:

$$100 \, m/m_0$$

in which:

m_0 represents the weight in grams of the test sample;

m represents the weight in grams of the copper contained in the test solution.

b) If the measurement was made with the color scale, the copper content, expressed in weight percent, is given by the formula:

if one used solution A:

$$\frac{0.000\,01\,(V - V_0)}{m_0} \times 100 = \frac{0.001\,(V - V_0)}{m_0}$$

if one uses solution B

$$\frac{0.000\,001\,(V - V_0)}{m_0} \times 100 = \frac{0.000\,1\,(V - V_0)}{m_0}$$

in which:

m_0 represents the weight in grams of the test sample;

V represents the number of milliliters of the standard solution that gave the same coloring as the solution to be analyzed;

V_0 represents the number of milliliters of the standard solution that gave the same coloring as the blank test.

5.7 Determination of the total copper content

5.7.1 Principle

Dissolution of the test sample in hydrofluoric acid and sulfuric acid, then volatilization of the silicon as the gaseous tetrafluoride.

Dissolution of all the metals of the residual test sample in hydrochloric acid, then dilution and spraying of the solution in the flame of an atomic absorption spectrometer, at a wavelength of 324.5 nm.

The method can be applied to the determination of copper contents up to 25 mg/kg.

5.7.2 Reagents

In the analysis, use only reagents of recognized analytical quantity, and distilled water or water of equivalent purity.

Warning: All necessary sanitary precautions and safety measures must be taken when using this method of analysis.

5.7.2.1 Acetylene under pressure.

5.7.2.2   Air under pressure.

5.7.2.3   Hydrochloric acid, 10% solution (weight/weight)

5.7.2.4   Hydrofluoric acid, 40% solution (weight/weight).
    (ρ_{20} = 1.13 g/mL).

5.7.2.5   Sulfuric acid, 98% solution (weight/weight)
    (ρ_{20} = 1.84 g/mL).

5.7.2.6   Copper, standard solution corresponding to 1 g/L of Cu
    Dissolve 1.000 g ± 0.001 g of very pure copper filings in a
mixture of 10 mL of water and 5 mL of nitric acid (ρ_{20} = 1.42
g/mL), contained in a 100-mL beaker. Boil under a fume hood in
order to eliminate the nitrogen oxides. Cool, transfer to a 1 L
volumetric flask, fill to that volume with water, and homogenize.
    1 mL of this standard solution contains 1,000 μg of copper.

5.7.2.7   Copper standard solution corresponding to 50 mg/L of Cu
    Using a pipette, remove 50.0 mL of the standard solution of
copper (5.7.2.6), and transfer to a 1-L volumetric flask, add
5 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with
water, and homogenize.
    1 mL of this standard solution contains 50 μg of copper.

5.7.2.8   Copper standard solution corresponding to 10 mg/L of Cu
    Using a pipette, remove 50.0 mL of the standard solution of
copper (5.7.2.7), and transfer to a 250-mL volumetric flask, add

1 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with water, and homogenize.

1 mL of this standard solution contains 10 μg of copper.

5.7.3 Equipment

The usual laboratory equipment and:

Platinum dish, capacity approximately 35 mL.

Atomic absorption spectrometer, equipped with an air-acetylene burner.

Analytical balance accurate to the nearest 0.001 g.

5.7.4 Procedure

5.7.4.1 Test sample

Weigh to the nearest 0.001 g approximately 2 g of sample in the platinum dish.

5.7.4.2 Blank test

In parallel to the determination and following the same procedure, do a blank test using the same quantities of all the reagents as those used for the determination but omitting the test sample.

5.7.4.3 Preparation of the calibration curve

5.7.4.3.1 Preparation of the reference solutions

In a series of six 50-mL volumetric flasks, introduce the volumes of standard copper solution indicated in the following table, and fill to that volume with water and homogenize.

Reference solutions for determination of the copper content

Volume of standard copper solution (5.7.2.8), mL	Corresponding copper content, $\mu g/mL$
0.5	0.1
2.5	0.5
5.0	1.0
10.0	2.0
15.0	3.0
25.0	5.0

5.7.4.3.2 Spectrometric measurements

Successively spray the reference solutions in the flame of the atomic absorption spectrometer and record the absorbance values at the wavelength of 324.5 nm, following the instructions of the manufacturer of the apparatus.

Spray water in the flame after each measurement.

5.7.3.3 Plotting the curve

Make a graph by plotting, for example, the copper contents in milligrams per milliliter on the abscissa and the corresponding absorbance values on the ordinate.

in which:

m_0 represents the weight in grams of the test sample;

V represents the number of milliliters of the standard solution that gave the same coloring as the solution to be analyzed;

V_0 represents the number of milliliters of the standard solution that gave the same coloring as the blank test.

5.7 Determination of the total copper content

5.7.1 Principle

Dissolution of the test sample in hydrofluoric acid and sulfuric acid, then volatilization of the silicon as the gaseous tetrafluoride.

Dissolution of all the metals of the residual test sample in hydrochloric acid, then dilution and spraying of the solution in the flame of an atomic absorption spectrometer, at a wavelength of 324.5 nm.

The method can be applied to the determination of copper contents up to 25 mg/kg.

5.7.2 Reagents

In the analysis, use only reagents of recognized analytical quantity, and distilled water or water of equivalent purity.

Warning: All necessary sanitary precautions and safety measures must be taken when using this method of analysis.

5.7.2.1 Acetylene under pressure.

5.7.2.2   Air under pressure.

5.7.2.3   Hydrochloric acid, 10% solution (weight/weight)

5.7.2.4   Hydrofluoric acid, 40% solution (weight/weight).
(ρ_{20} = 1.13 g/mL).

5.7.2.5   Sulfuric acid, 98% solution (weight/weight)
(ρ_{20} = 1.84 g/mL).

5.7.2.6   Copper, standard solution corresponding to 1 g/L of Cu
      Dissolve 1.000 g ± 0.001 g of very pure copper filings in a
mixture of 10 mL of water and 5 mL of nitric acid (ρ_{20} = 1.42
g/mL), contained in a 100-mL beaker. Boil under a fume hood in
order to eliminate the nitrogen oxides. Cool, transfer to a 1 L
volumetric flask, fill to that volume with water, and homogenize.
      1 mL of this standard solution contains 1,000 μg of copper.

5.7.2.7   Copper standard solution corresponding to 50 mg/L of Cu
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copper (5.7.2.6), and transfer to a 1-L volumetric flask, add
5 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with
water, and homogenize.
      1 mL of this standard solution contains 50 μg of copper.

5.7.2.8   Copper standard solution corresponding to 10 mg/L of Cu
      Using a pipette, remove 50.0 mL of the standard solution of
copper (5.7.2.7), and transfer to a 250-mL volumetric flask, add

1 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with water, and homogenize.

1 mL of this standard solution contains 10 μg of copper.

5.7.3 Equipment

The usual laboratory equipment and:

Platinum dish, capacity approximately 35 mL.

Atomic absorption spectrometer, equipped with an air-acetylene burner.

Analytical balance accurate to the nearest 0.001 g.

5.7.4 Procedure

5.7.4.1 Test sample

Weigh to the nearest 0.001 g approximately 2 g of sample in the platinum dish.

5.7.4.2 Blank test

In parallel to the determination and following the same procedure, do a blank test using the same quantities of all the reagents as those used for the determination but omitting the test sample.

5.7.4.3 Preparation of the calibration curve

5.7.4.3.1 Preparation of the reference solutions

In a series of six 50-mL volumetric flasks, introduce the volumes of standard copper solution indicated in the following table, and fill to that volume with water and homogenize.

Reference solutions for determination of the copper content

Volume of standard copper solution (5.7.2.8), mL	Corresponding copper content, $\mu g/mL$
0.5	0.1
2.5	0.5
5.0	1.0
10.0	2.0
15.0	3.0
25.0	5.0

5.7.4.3.2 Spectrometric measurements

Successively spray the reference solutions in the flame of the atomic absorption spectrometer and record the absorbance values at the wavelength of 324.5 nm, following the instructions of the manufacturer of the apparatus.

Spray water in the flame after each measurement.

5.7.3.3 Plotting the curve

Make a graph by plotting, for example, the copper contents in milligrams per milliliter on the abscissa and the corresponding absorbance values on the ordinate.

5.7.4.4   Determination

5.7.4.4.1 Preparation of the test solution

Add 10 mL of the hydrofluoric acid solution (5.7.2.4) and 0.5 mL of the sulfuric acid solution (5.7.2.5) to the test sample (5.7.4.1) in the dish.

Place the dish with its contents on a heated sand bath and evaporate, using a fume hood, until the release of the white fumes of sulfuric acid stops.

Dissolve any residue in 5 mL of hydrochloric acid (5.7.2.3) and transfer to a 10 mL volumetric flask. Fill to that volume with water, then transfer the solution to a dry polyethylene bottle.

5.7.4.4.2 Spectrometric measurements

Spray the test solution (5.7.4.4.1) and the blank test solution in the flame of the atomic absorption spectrometer, and measure the absorbance values at 324.5 nm, following the instructions of the manufacturer of the apparatus. Repeat this procedure and record the average absorbance values of the test solution and of the blank test solution.

Spray water in the flame after each measurement.

5.7.5   Expression of the results

Referring to the calibration curve, determine the copper contents that correspond to the absorbance values of the test solution and of the blank test solution.

The total copper content of the sample, expressed in milligrams per kilogram, is given by the formula:

$$10(m_1 - m_2)/m$$

in which:

m_1 is the copper content, in micrograms per milliliter, of the test solution;

m_2 is the copper content, in micrograms per milliliter, of the blank test solution;

m is the weight in grams of the test sample.

Express the result to the nearest 0.1 mg/kg.

5.8   Determination of the total manganese content

5.8.1   Principle

Proceed as in the determination of the copper content (see 5.7.1), except that the absorbance value of the test solution is measured at 279.5 nm and is compared with the absorbance values of reference solutions of manganese.

The method can be applied to the determination of manganese contents up to 250 mg/kg.

5.8.2   Reagents

In the analysis, use only reagents of recognized analytical quality, and distilled water or water of equivalent purity.

Warning: All necessary sanitary precautions and safety measures must be taken when using this method of analysis.

5.8.2.1   Acetylene under pressure.

5.8.2.2   Air under pressure.

5.8.2.3   Hydrochloric acid, solution
     See paragraph 5.7.2.3.

5.8.2.4   Hydrofluoric acid, solution.
     See paragraph 5.7.2.4.

5.8.2.5   Sulfuric acid, solution
     See paragraph 5.7.2.5.

5.8.2.6   Manganese, standard solution corresponding to 1 g/L of Mn

     Dissolve 1.000 g $\pm$ 0.001 g of very pure manganese free of oxide in a mixture of 50 mL of water and 5 mL of nitric acid (ρ_{20} = 1.42 g/mL), contained in a 100-mL beaker. Boil under a fume hood in order to eliminate the nitrogen oxides. Cool, transfer to a 1-L volumetric flask, fill to that volume with water, and homogenize.

     1 mL of this standard solution contains 1,000 μg of manganese.

5.8.2.7   Manganese, standard solution corresponding to 50 mg/L of Mn

     Using a pipette, remove 50.0 mL of the standard solution of manganese (5.8.2.6), and transfer to a 1-L volumetric flask, add 5 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with water, and homogenize.

     1 mL of this standard solution 50 μg of manganese.

5.8.2.8   Manganese, standard solution corresponding to 10 mg/L of Mn

Using a pipette, remove 50.0 mL of the standard solution of manganese (5.8.2.7), and transfer to a 250-mL volumetric flask, add 1 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with water, and homogenize.

1 mL of this standard solution 10 μg of manganese.

5.8.3   Equipment
As specified in chapter 5.7.3.

5.8.4   Procedure

5.8.4.1   Test sample
See paragraph 5.7.4.1.

5.8.4.2   Blank test
See paragraph 5.7.4.2.

5.8.4.3   Preparation of the calibration curve

5.8.4.3.1 Preparation of the reference solutions
In a series of six 50-mL volumetric flasks, introduce the volumes of standard manganese solution (5.8.2.8) indicated in the following table, and fill to that volume with water and homogenize.

Reference solutions for determination of the manganese content

Volume of standard Mn solution (5.8.2.8), mL	Corresponding Mn content, μg/mL
0.5	0.1
2.5	0.5
5.0	1.0
10.0	2.0
15.0	3.0
25.0	5.0

5.8.4.3.2 Spectrometric measurements

Successively spray the reference solutions in the flame of the atomic absorption spectrometer and record the absorbance values at the wavelength of 279.5 nm, following the instructions of the manufacturer of the apparatus.

5.8.4.3.3 Plotting the curve

Make a graph by plotting, for example, the manganese contents in milligrams per milliliter on the abscissa and the corresponding absorbance values on the ordinate.

5.8.4.4   Determination

5.8.4.4.1 Preparation of the test solution

See paragraph 5.7.4.4.1.

5.8.4.4.2 Spectrometric measurements

Spray the test solution and the blank test solution in the flame of the atomic absorption spectrometer, and measure the absorbance values at 279.5 nm, following the instructions of the manufacturer of the apparatus. Repeat this procedure and record the average absorbance values of the test solution and of the blank test solution.

Spray water in the flame after each measurement.

If the absorbance value of the test solution is greater than that of the reference solution with the highest manganese content, dilute 5 mL of the test solution with water in order to produce 50 mL, repeat the measurement, and take into account the dilution in the expression of the results.

5.8.5   Expression of the results

Referring to the calibration curve, determine the manganese contents corresponding to the absorbance values of the test solution and of the blank test solution.

The total manganese content of the sample, expressed in milligrams per kilogram, is given by the formula:

$$10(m_3 - m_4)/m$$

in which:

m_3 is the manganese content, in micrograms per milliliter, of the test solution;

m_4 is the manganese content, in micrograms per milliliter, of the blank test solution;

m is the weight in grams of the test sample.

Note: if the test solution was diluted as described in 5.8.4.4.2, multiply the factor of the formula by 10.

Express the result to the nearest 0.1 mg/kg.

5.9 Determination of the total iron content

5.9.1 Principle

The principle is the same as for the determination of the copper content (see 5.7.1), except that the absorbance value of the test solution is measured at 248.3 nm and is compared with the absorbance values of reference solutions of iron.

The method can be applied to the determination of iron contents up to 500 mg/kg.

5.9.2 Reagents

In the analysis, use only reagents of recognized analytical quality, and distilled water or water of equivalent purity.

Warning: All necessary sanitary precautions and safety measures must be taken when using this method of analysis.

5.9.2.1 Acetylene under pressure.

5.9.2.2 Air under pressure.

5.9.2.3 Hydrochloric acid, solution

See paragraph 5.7.2.3.

5.9.2.4   Hydrofluoric acid, solution.
    See paragraph 5.7.2.4.

5.9.2.5   Sulfuric acid, solution
    See paragraph 5.7.2.5.

5.9.2.6   Iron, standard solution corresponding to 1 g/L of Fe
    Dissolve 1.000 g $\pm$ 0.001 g of very pure iron in a mixture of 10 mL of water and 5 mL of nitric acid (ρ_{20} = 1.42 g/mL), contained in a 100-mL beaker. Boil under a fume hood in order to eliminate the nitrogen oxides. Cool, transfer to a 1-L volumetric flask, fill to that volume with water, and homogenize.
    1 mL of this standard solution contains 1,000 μg of iron.

5.9.2.7   Iron, standard solution corresponding to 50 mg/L of Fe
    Using a pipette, remove 50.0 mL of the standard solution of iron (5.9.2.6), and transfer to a 1-L volumetric flask, add 5 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with water, and homogenize.
    1 mL of this standard solution contains 50 μg of iron.

5.9.2.8   Iron, standard solution corresponding to 10 mg/L of Fe
    Using a pipette, remove 50.0 mL of the standard solution of iron (5.9.2.7), and transfer to a 250-mL volumetric flask, add 1 mL of nitric acid (ρ_{20} = 1.42 g/mL), fill to that volume with water, and homogenize.
    1 mL of this standard solution contains 10 μg of iron.

5.9.3   Equipment

As specified in chapter 5.7.3.

5.9.4   Procedure

5.9.4.1   Test sample

See paragraph 5.7.4.1.

5.9.4.2   Blank test

See paragraph 5.6.5.

5.9.4.3   Preparation of the calibration curve

5.9.4.3.1 Preparation of the reference solutions

In a series of six 50-mL volumetric flasks, introduce the volumes of standard iron solution (5.9.2.8) indicated in the following table, and fill to that volume with water and homogenize.

Reference solutions for determination of the iron content

Volume of standard iron solution (5.9.2.8), mL	Corresponding iron content, $\mu g/mL$
0,5	0,1
2,5	0,5
5,0	1,0
10,0	2,0
15,0	3,0
25,0	5,0

5.9.4.3.2 Spectrometric measurements

Successively spray the reference solutions in the flame of the atomic absorption spectrometer and record the absorbance values at the wavelength of 248.3 nm, following the instructions of the manufacturer of the apparatus.

Spray water in the flame after each measurement.

5.9.4.3.3 Plotting the curve

Make a graph by plotting, for example, the iron contents in milligrams per milliliter on the abscissa and the corresponding absorbance values on the ordinate.

5.9.4.4   Determination

5.9.4.4.1 Preparation of the test solution

See paragraph 5.7.4.4.1.

5.9.4.4.2 Spectrometric measurements

Spray the test solution and the blank test solution in the flame of the atomic absorption spectrometer, and measure the absorbance values at 248.3 nm, following the instructions of the manufacturer of the apparatus. Repeat this procedure and record the average absorbance values of the test solution and of the blank test solution.

Spray water in the flame after each measurement.

If the absorbance value of the test solution is greater than that of the reference solution with the highest iron content, dilute 5 mL of the test solution with water in order to produce

100 mL, repeat the measurement, and take into account the dilution in the expression of the results.

5.9.5   Expression of the results

Referring to the calibration curve, determine the iron contents corresponding to the absorbance values of the test solution and of the blank test solution.

The total iron content of the sample, expressed in milligrams per kilogram, is given by the formula:

$$10(m_5 - m_6)/m$$

in which:

m_5 is the iron content, in micrograms per milliliter, of the test solution;

m_6 is the iron content, in micrograms per milliliter, of the blank test solution;

m is the weight in grams of the test sample.

Note: if the test solution was diluted as described in 5.9.4.4.2, multiply the factor of the formula by 20.

Express the result to the nearest 0.1 mg/kg.

5.10 Determination of the conductivity of a suspension of silica in water

5.10.1   Definitions
Electrical resistance   See NF X 01-205
Electrical conductance   See NF X 02-205
Electrical resistivity   See NF X 02-205
Electrical conductivity   See NF X 02-205

5.10.2   Principle

Measurement of the electrical resistance or conductance of a column of water delimited by two platinum electrodes (or electrodes covered with platinum black) maintained parallel.

If R is the resistance of the column of water in ohms, S the cross section in centimeters squared, and l its length in centimeters:

- the electrical resistivity, in ohm-centimeters is equal to R x S/l,

- the electrical conductivity, in siemens per centimeter, is equal to 1/R x l/S.

l/S is called the "measuring element constant," and is most often expressed in reciprocal centimeters (cm^{-1}) (form of expression accepted by ISO Recommendation 31/0).

The resistivity (or conductivity) varies with temperature. The reference temperature for the expression of the resistivity or of the conductivity is 20°C. The conductivity γ_1 at temperature t_1 is related to the conductivity γ_2 at temperature t_2 by the equation:

$$\gamma_1 = \gamma_2 [1 + \alpha (t_1 - t_2)]$$

in which α is a coefficient that depends on the nature and concentration of the elements contained in the water.

5.10.3   Reagents

5.10.3.1 Distilled water

Add to water that has already been subjected to a first distillation 0.5 g/L of sulfuric acid (ρ_{20} = 1.84 g/mL) and distill again. Collect only the second third of the distillate and measure its conductivity at least three times at 60-min intervals: the water is suitable if its conductivity remains constant and is not higher than 200 μS/m at 20°C.

5.10.3.2 Potassium chloride - standard solutions

Using analytically pure potassium chloride, in powder form or in fine crystals, previously dried to a constant weight at a temperature of 105°C $\pm$ 2°C, prepare three standard solutions c(KCl) = 0.1 mol/L; c(KCl) = 0.01 mol/L and c(KCl) = 0.001 mol/L.

5.10.3.2.1 Solution c(KCl) = 0.1 mol/L: Dissolve 7.4558 g $\pm$ 0.0005 g of potassium chloride in distilled water (5.10.3.1). Then fill to 1 L with distilled water at 20°C $\pm$ 2°C.

5.10.3.2.2 Solution c(KCl) = 0.01 mol/L: Dissolve 0.7456 g $\pm$ 0.0005 g of potassium chloride in distilled water (5.10.3.1). Then fill to 1 L with distilled water at 20°C $\pm$ 2°C.

5.10.3.2.3 Solution c(KCl) = 0.001 mol/L: Prepare the solution just before use by dilution of 100 mL of the solution (5.10.3.2.2) to 1 L with distilled water (5.10.3.1).

Keep the solutions in polyethylene bottles provided with tight stoppers.

The electrical resistivity and conductivity values at 20°C of the potassium chloride in these three solutions are the following:

Concentration of KCl, mol/L	Resistivity (Ωcm) (1)	Conductivity (μ Scm^{-1}) (1)
0.1	85.62	11 680 (2)
0.01	783.1	1 277 (2)
0.001	7 299	137
(1) The resistivity or the conductivity of the water (5.10.3.1) used for preparing the solutions is not included in these values.		
(2) Value taken from Information bulletin No. 2 - IUPAC Catalog of Physicochemical Standard Substances (December 1969).		

5.10.4   Equipment

5.10.4.1 Conductimeter

The essential element of the commercialized conductimeters is generally a Wheatstone bridge supplied with alternating current voltage in order to avoid variations in the composition of the tested solutions (polarization effect). Certain conductimeters are equipped with a temperature compensation device which, by direct reading, allows one to obtain a good assessment of the resistivity at the reference temperature, provided that the temperature of the tested water does not differ

excessively from this reference temperature. Certain apparatuses allow one to measure the electrical resistance and others allow one to measure the electrical conductance.

5.10.4.2 Measuring element

In practice, consisting of two electrodes covered with platinum or platinum black, each having a surface area on the order of 1 cm^2, which are maintained parallel approximately 1 cm apart, and which are protected by a glass sheath (allowing for a good exchange between the solution and the electrodes).

Follow the instructions of the supplier in order to clean this measuring element. Keep it in water (5.10.3.1) when it is not in use.

This measuring element generally constitutes one of the branches of the Wheatstone bridge, allowing one to determine the value of the resistance (or of the conductance) of the column of liquid between the electrodes of the immersed measuring element.

5.10.4.3 Precision thermometer EPL/0.1-5/25 NF B 35-504

Water bath at 20°C ± 0.1°C if the conductimeter is not equipped with a temperature compensation device.

5.10.5 Procedure

5.10.5.1 Preliminary considerations

Follow the indications of the information for use of the conductimeter which is used, for putting the apparatus in operating condition. As a general rule:

- choose a measuring element with a high constant for water that is a good conductor, and on the contrary, choose a measuring element with a low constant for water that is a poor conductor;

- use a measurement frequency such that it does not lead to phenomena of polarization on the electrodes: a measurement frequency greater than or equal to 1,000 Hz is recommended for solutions that are good conductors.

5.10.5.2 Determination of the constant of the measuring element

For rapid verification of the constant of the measuring element, compare the values obtained for the resistivity or the conductivity of the same solution at the same temperature with the measuring element to be verified and a standard measuring element whose constant is precisely known. To do this, use a solution whose nature is as similar as possible to that of the waters that will be examined later.

For a direct determination of the constant of the measuring element, use one of the standard solutions of potassium chloride (5.10.3.2):

- rinse the measuring element clean several times with distilled water (5.10.3.1) and then at least twice with the standard solution of potassium chloride (5.10.3.2) whose conductivity is closest to that of the solution to be measured.

- then, bring the standard solution of potassium chloride to 20°C ± 0.1°C, and measure the resistance (or the conductance) of the measuring element in the presence of fractions of this solution which are renewed each time, until the readings remain constant to the nearest 0.2%. Make sure that there are no gas

bubbles trapped in the measuring element, and particularly in contact with the electrodes.

The constant J of the measuring element in reciprocal centimeters is given by the formula:

$$J = R_{KCl} (\gamma_{KCl} + \gamma_{H_2O})$$

in which:

R_{KCl} is the measured resistance expressed in microhms;

γ_{KCl} is the conductivity of the potassium chloride in the standard solution of potassium chloride that was used, expressed in microsiemens per centimeter;

γ_{H_2O} is the conductivity of the distilled water for the preparation of the standard solution of potassium chloride. This value can be neglected if it is small in relation to γ_{KCl} (that is to say if neglecting it does not introduce an error greater than 0.1%).

5.10.5.3 Determination of the conductivity of the suspension of silica

5.10.5.3.1   Preparation of the suspension of silica

Weigh 5 g of silica sample to the nearest 0.01 g.

Add 100 mL of permuted [sic; possibly, deionized] water.

Stir vigorously.

Bring to a boil.

Cool to room temperature (20-25°C).

Readjust to 100 mL.

Note: This preparation of the suspension is identical to that for the measurement of the pH. It is therefore possible, in a single operation, to successively measure the pH and the conductivity.

5.10.5.3.2   Measurement

Rinse the measuring element clean several times with distilled water (5.10.3.1), and then introduce it in the suspension to be examined. The measurement is made with stirring (magnetic bar). The measurement must be stable. Make sure that there are no gas bubbles trapped in the measuring element and particularly in contact with the electrodes.

For very precise measurements, bring the tested suspension to 20°C $\pm$ 0.1°C.

5.10.6   Expression of the results

Indicate the conductivity at 20°C expressed in siemens per centimeter or in an appropriate lower multiple.

5.10.7   Note: The conductivity of a silica suspension is generally a function of the content in terms of soluble salts.

5.11 Determination of the specific surface area by nitrogen adsorption

Note: Two methods are presented:

- gravimetric method,

- method with one point [sic] by chromatography.

These two methods are based on the studies of Brunauer, Emmet, and Teller (J. Am. Chem. Soc. 60, 309, 1938) relating to

adsorption in a multimolecular layer. The BET theory proposed by these authors allows one access to the total specific surface area (or area per unit of weight) of a powder.

The gravimetric method requires one to measure the quantity of nitrogen adsorbed for different partial pressures in the domain of validity of the BET theory.

The gravimetric method is the stricter method and constitutes the reference method.

The principle of the gravimetric method is described in detail in the chapter relating to this method.

The documentation section X 11-622 presents a more complete description of the principle of the method with one point·by chromatography.

5.11.1   Gravimetric method

5.11.1.1 Principle - theory

The phenomenon of adsorption is observed when a gas is put in contact with a solid body: Some of the molecules of adsorbate disappear from the gaseous phase and become attached to the surface of the solid.

Depending on the nature of the bonds between the surface atoms of the solid and the atoms of the adsorbed gas, two types of adsorption are distinguished:

- physical adsorption, in which the forces of interaction are of a physical nature (van der Waals),

- chemical adsorption, in which chemical bonds form between the surface atoms and the adsorbed atoms or molecules.

In chemical adsorption, the surface is lined with at most a monomolecular layer. On the contrary, in physical adsorption, a multimolecular layer can form.

Physical adsorption is an equilibrium condition that depends on temperature: the condensation of the gaseous molecules on the surface of the solid is promoted by reducing the temperature. The phenomenon is described by an adsorption isotherm which represents the quantity of gas adsorbed on the solid as a function of the pressure. The specific surface area of the solid is necessarily involved in the equation of this isotherm; one thus has a way of measuring it.

Brunauer, Emmet and Teller established an equation that represents the isotherm of physical adsorption, taking as starting hypotheses:

1 - the phenomenon is pure physical adsorption (only van der Waals attractions);

2 - the surface of the solid is energetically homogeneous;

3 - the lateral interactions between adsorbed molecules are negligible;

4 - the number of layers adsorbed is unlimited;

5 - the polymolecular layers are constantly present.

This equation has the form:

$$\frac{P}{V(P_0 - P)} = \frac{1}{C V_m} + \frac{C-1}{C V_m}\ \frac{P}{P_0}$$

with:

V = volume adsorbed at equilibrium under pressure P;

V_m = volume of gas necessary for establishment of a monomolecular layer;

P = pressure at equilibrium;

P_0 = vapor pressure at saturation of the adsorbate at the temperature of the experiment;

P/P_0 = relative pressure;

C = constant characterizing the energy of adsorbate-adsorbent interaction.

In plotting the variations of $P/V(P_0 - P)$ as a function of P/P_0, one must therefore obtain a line called the "BET line:"

- with ordinate at the origin $\alpha = 1/C \cdot V_m$; hence, $V_m = 1/\alpha C$;

- with slope $\beta = (C - 1)/C \cdot V_m$; hence, $C = 1 + (\beta/\alpha)$.

Knowledge of the volume of gas necessary for covering the solid with a monomolecular layer then allows one to calculate the specific surface area S of the sample:

$$S = \frac{1}{m} \; N \cdot a_s \cdot \frac{V_m}{VM}$$

with:

m = weight of the sample;

N = Avogadro's number;

a_s = area effectively occupied by a molecule of adsorbate;

VM = molar volume of the adsorbate.

In the most frequent cases, the adsorbate used is nitrogen, and the experiment is done at 77 K (temperature of a liquid nitrogen bath at atmospheric pressure). Under these conditions, the preceding constants have the value:

$$a_s = 0.162 \ nm^2$$
$$VM = 22,414 \ cm^3/mol$$

hence:

$$S = \frac{1}{m} \ 4.35 \ V_m$$

with V_m expressed in cubic centimeters of gaseous nitrogen at STP, m expressed in grams, and S in meters squared per gram.

5.11.1.2 Methodology

5.11.1.2.1 Equipment

The essential part of the equipment consists of a balance whose assembly is diagrammed in Figure 2.

It is beam balance articulated on a torsion band and functioning with zero deviation. An optical flap solidly connected with the beam partially blacks out the light beam from a microlamp that lights two stationary photocells.

The rebalancing reequilibration of the beam is done using two stationary solenoids that receive a stabilized compensation current generated by the signal from the photocells. The recording of this current, proportional to the variation of the weight of the sample, expresses the change of the phenomenon

which is studied. The perfectly symmetrical design of the assembly makes it possible to minimize perturbations from static and dynamic thrusts[1].

The pumping unit consists of a primary vane pump, a secondary oil diffusion pump, and a liquid nitrogen cryogenic trap.

The complete assembly is described in Figure 3.

5.11.1.2.2   Procedure

Three successive phases can be distinguished:

- sample removal and weighing;

- pretreatment of the sample (elimination of the physically adsorbed water;

- adsorption and desorption of the adsorbate.

a) Weighing of the sample

The weight of the sample is on the order of 15 mg for a powdered solid with a specific surface area between 100 m^2/g and 200 m^2/g.

The sensitivity of the balance is adjusted to approximately 5 mV/mg. A first balancing of this balance is done by putting a boat of glass balls whose weight is similar to the weight of the sample on the reference plate, and an empty boat on the sample plate.

----

[1]As an example of a balance module to be used, one can mention the module MTB-10-8 manufactured by the company Setaram at Caluire-69300.

This boat is then taken and weighed on a balance accurate to the nearest 1/10 mg. One then introduces a quantity of solid in the vicinity of 15 mg and weighs the boat again. By double weighing, one therefore obtains the exact weight of the moist solid, m_H.

The sample holding boat is again hung on the plate of the balance (Figure 2). The preceding balance is obviously upset, and it is reestablished by means of the electromagnetic tare weight (ETW); which allows one to know the weight of solid introduced into the boat. One can thus compare the values obtained with the two balances. In general, the difference does not exceed 1.5%.
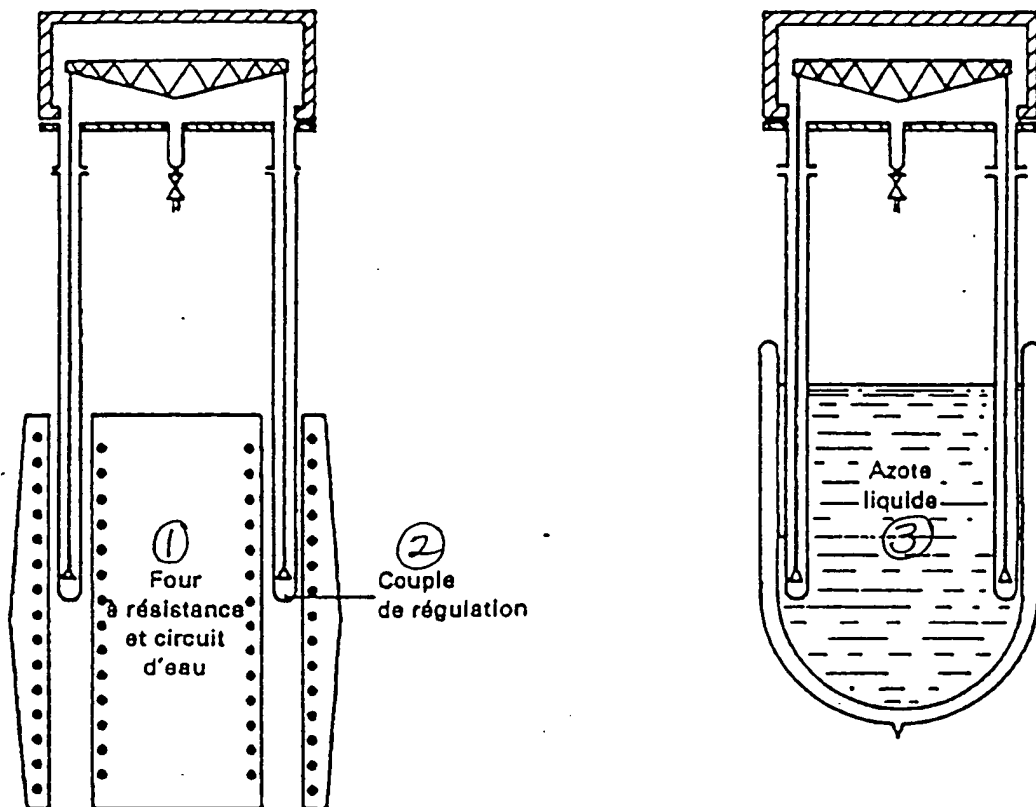
Figure 2

Key: 1   Resistance furnace and water circulation
      2   Regulating moment
      3   Liquid nitrogen

53

① Bouteille d'azote	⑨ Capteur de pression P_o
② Électro-vanne d'injection d'azote	⑩ Vase Dewar d'azote liquide à niveau constant
③ Électro-vanne de tirage au vide	⑪ Pompe à vide à diffusion d'huile
④ Capteur de pression P	⑫ Pompe à vide à palette
⑤ Robinet de tirage rapide au vide	⑬ Micro-ordinateur
⑥ Piège à azote liquide	⑭ Interfaces du calculateur
⑦ Piège à carboglace	⑮ Voltmètre numérique avec multiplexeur
⑧ Microbalanc	⑯ Boîte à relais

Figure 3

Key: 1   Bottle of nitrogen
     2   Electrovalve for nitrogen injection
     3   Electrovalve for drawing the vacuum
     4   Pressure P sensor
     5   Tap for rapidly drawing the vacuum
     6   Liquid nitrogen trap
     7   Dry ice trap
     8   Microbalance
     9   Pressure P_0 sensor
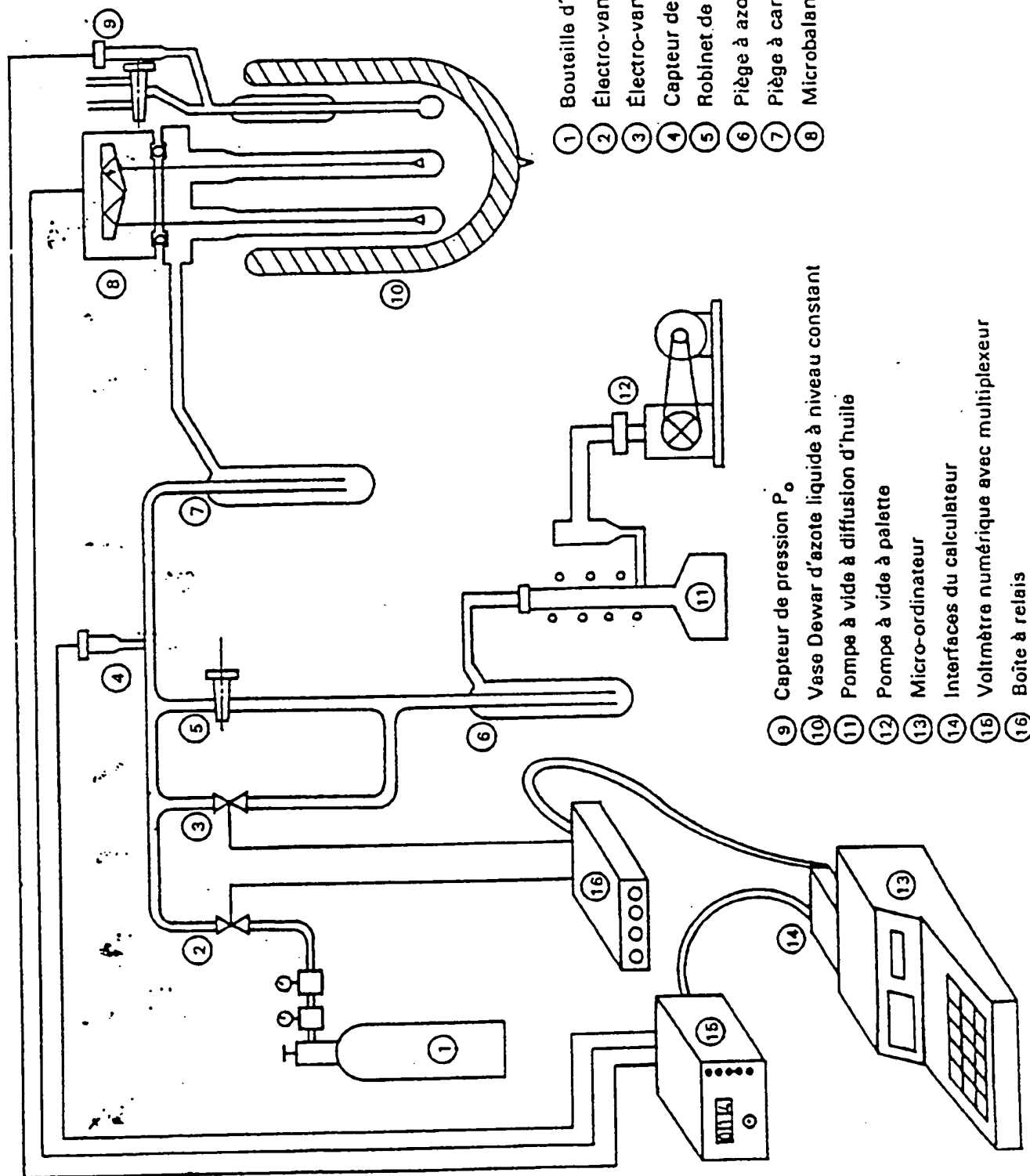   10 Dewar vessel of liquid nitrogen at constant level
     11 Oil diffusion vacuum pump
     12 Vane vacuum pump
     13 Microcomputer
     14 Interfaces of the calculator
     15 Digital voltmeter with multiplexor
     16 Relay box

b) Thermal treatment of the sample

The BET theory assumes that the surface of the adsorbent solid is energetically homogeneous. It is therefore necessary to rid it of adsorbed products, making sure not to basically modify the surface condition.

The procedure is as follows.

- [The sample is] put under secondary vacuum at room temperature. This operation must be done gradually; approximately 30 min is needed to reach a pressure on the order of 1 Pa.

- One then observes a weight loss of the sample corresponding to adsorption of water. The sample is maintained under dynamic vacuum P < 0.1 Pa at room temperature until a constant weight is obtained.

- In order to complete this degassing, one then heats the sample up to 150°C at a rate of 2°/min. One again observes a

weight loss, and the temperature is regulated at 150°C until stabilization of the weight of the sample (2 to 3 h are necessary).

- The heating is then interrupted, and it is allowed to cool naturally to room temperature.

- Finally, the two tubes of the balance are immersed in a liquid nitrogen bath so that the boats are at a depth of 15 cm below the surface of the liquid nitrogen (see Figure 2). During the rest of the experiment, the level of liquid nitrogen should be maintained constant within a millimeter using an automatic system of injection controlled by a thermoresistant sensor.

- Starting from the time of immersion, it is necessary to allow the temperature to equilibrate for a minimum of 30 min.

All the sample pretreatment operations before nitrogen adsorption require approximately 5 h. The balance allows one to constantly follow the change in weight of the sample; one thus knows the loss of weight m resulting from degassing and therefore the weight of dry silica, m_s:

$$m_s = mH - \Delta m$$

This is the value which is used in the calculation of the specific surface area of the sample.

c) Measurement of the vapor pressure at saturation P_0

The phases of adsorption and desorption of the nitrogen require 10 to 15 h. In such a timespan, the atmospheric pressure can undergo extensive fluctuations; hence, variations of the liquid nitrogen bath and, consequently, nonnegligible variations of the vapor pressure at saturation P_0 (several millimeters of

mercury) [can occur]. The condensation of moisture and of oxygen in the liquid nitrogen bath also contributes to these variations.

It is therefore absolutely necessary to check the vapor pressure at saturation of the adsorbate throughout the experiment. To do this, one continually measures the pressure predominating in a reference enclosure containing condensed nitrogen. The spherical reservoir is immersed in the liquid nitrogen bath in the vicinity of the boats of the balance (see Figure 2). The filling of this reservoir of liquid nitrogen is done by condensation of gaseous nitrogen; this operation obviously requires one to have made a vacuum in the spherical reservoir beforehand.

b) [sic; d] Adsorption-desorption isotherm

The whole experiment is now managed by a microcalculator, which receives the information coming from:

- the balance of the type defined in paragraph 5.11.1.2.1;
- a sensor that measures the pressure P predominating in the enclosure;
- a second sensor that measures the pressure P_0 in the reference bulb where liquid nitrogen is condensed.

This information is transmitted through a multiplexor, an AOIP voltmeter, and an interface, for example, GP 10.

The calculator controls the opening and closing of the two electrovalves by the intermediary of an interface, for example, IEE, and a relay box. These two valves allow one either to introduce nitrogen into the enclosure or to connect it with the pumping unit for describing the desorption isotherm.

In a simplified manner, the driving software carries out the following operations:

- opening of one of the two electrovalves for time t;
- every minute, scanning of the values of the weight m of the sample, of the pressure P in the enclosure, and of the saturating vapor pressure P_0;
- filtering of the signals through 7 consecutive points;
- equilibrium test on 5 consecutive filtered points;
- if the equilibrium test is satisfactory both for the weight and for the pressure, acquisition and filing of the values of values of m, P, and P_0;
- opening of one of the two electrovalves to reach the next point. The duration of opening of the injection valve increases with the pressure P, whereas the duration of the opening of the pumping valve decreases with the pressure P; this is in order to obtain roughly constant increments.

The domain of pressure investigated is $0 < P/P_0 < 0.96$; some fifty experimental points are acquired in order to describe the adsorption isotherm, and some forty for the desorption isotherm.

The use of the complete "adsorption + desorption" isotherm enables one to collect information as to the texture of the solid (distribution of the pores with diameter less than 50 nm).

For calculating the BET surface area only, only the adsorption points acquired in the domain $0 < P/P_0 < 0.40$ are necessary; one can therefore possibly limit the experiment to the investigation of this domain of relative pressure if one does not wish to obtain more information as to the texture of the sample.

5.11.1.2.3   Calculation of the BET surface area

It is generally accepted that the domain of validity of the BET theory is: $0.05 < P/P_0 < 0.35$. In fact, depending on the nature of the material studied, this domain can be more restricted or less restricted. It is therefore necessary to look for the true domain of linearity.

This is done using a software based on the Fischer-Snedecor test (see NF X 06-065). The main steps of the calculation are the following:

1 - reading in the file of all the experimental points acquired during the phase of adsorption in the domain of relative pressure $0.04 < P/P_0 < 0.40$ (15 to 20 points);

2 - calculation of the regression curve by the least squares method;

3 - calculation of the parameters of the second degree polynomial by the least squares method;

4 - calculation of the coefficient F, which is the difference between the sum of the residual squares obtained by the first-order fit and the sum of the residual squares obtained by the second-order fit, divided by the residual mean square;

5 - Fischer-Snedecor test: comparison of F and F_0 of Fischer-Snedecor at the two-tailed 95% probability threshold:

• If $F < F_0$: The improvement contributed by a second-order fit is not significant. Pass to point 7;

• If $F > F_0$: The fit of the second-order polynomial is significantly better. Pass to point 6;

6 - elimination of the point at which the absolute difference between the experimental value and the value

calculated by the regression curve is the greatest. Return to point 2 (A test provides for obligatory stopping of the calculation loop if there are only 5 experimental points remaining for fitting the BET line.);

7 - calculation of the monomolecular volume and of the constant C from the parameters of the regression line;

8 - calculation of the 95% confidence intervals from the standard deviations of the slope and of the ordinate at the origin weighted by the quantity $t_{0.975;n-2}$ of the distribution of Student's t at (n - 2) degrees of freedom (n = the number of experimental points used to fit the BET line);

9 - coherence tests; four tests are done:

- Is the BET line fitted over more than 5 experimental points?
- Is the ordinate at the origin positive?
- Is the calculated monomolecular volume framed by the experimental points of the linear domain?
- Is the relative pressure corresponding to the monomolecular layer

$$\left(P/P_o = \frac{\sqrt{c}-1}{c-1} \right)$$

in the linear domain?

10 - issuing of the results with a different presentation depending on whether the coherence tests are satisfied or not.

- The program presented in Appendix A is designed for an HP 85 microcalculator equipped with an HP 7470 A plotting table (HP-

IB82 037 A interface)[2]. The experimental points are stored in the file in the form of pairs (P2(i), W(i) with:

- P2(i) = relative pressure P/P_0 of the ith point,
- W(i) = volume per unit of weight of adsorbed nitrogen in cubic centimeters (STP) per gram.

• Appendix B illustrates the results obtained on the plotting table.

Notes: - If one of the coherence tests is not satisfied, this is an indication of an unsatisfactory application of the BET model. This often comes from excess heterogeneity of the surface of the sample, heterogeneity which may itself result from degassing conditions that are not completely optimized for the type of material studied.

- The experimental points produced for relative pressures $P/P_0 < 0.04$ are not taken into account in the search for the domain of linearity, and consequently, in the calculation of the BET surface area. It is however absolutely necessary to produce at least two experimental points in this domain of pressure; this is for the purpose of facilitating putting the sample at thermal equilibrium with the liquid nitrogen bath. This precaution is most particularly important for materials that are poor heat conductors.

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[2]Any other type of microcalculator equipped with an interface and an appropriate plotting table can be used, however. It is appropriate in this case to modify the program appearing in Appendix A in order to adapt it to the basic language specific to the microcalculator.

5.11.2   Method with 1 point by chromatography

5.11.2.1 Principle

One determines the quantity of gas adsorbed by the sample, which is maintained at a suitable temperature, through a measurement of variation of concentration of the adsorbate (nitrogen) in a carrier gas (helium).

5.11.2.2 Equipment

The apparatus used must allow one to automatically perform a BET determination with 1 point by variation of the thermal conductivity of a gaseous mixture formed by a carrier gas, helium, and an adsorbent gas, nitrogen[3].

Two gaseous mixtures can be chosen, either 10% nitrogen in 90% helium or 30% nitrogen in 70% helium.

The criterion for choosing will be a function of the constant C which describes the energy of interaction between the adsorbent gas and the surface which is studied.

5.11.2.3 Preparation of the sample

- In a glass cell, weigh between 100 mg and 200 mg of product to be tested.

- Put the cell on a cell holder, lock this cell holder on the degassing station.

- Activate the degassing station.

- Establish a circulation of nitrogen of 15 mL/min.

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[3]The BETA 2000 apparatus of the company Beta Scientific corresponds to this description.

- Position the heating mantle around the cell; adjust the heating potentiometer in order to obtain 190°C.

The duration of drying is set at 2 h at 190°C.

After drying:

- cut off the heating and the nitrogen circulation,

- remove the heating mantle,

- disconnect the cell and its cell holder from the degassing station; the dried product is automatically isolated in the cell.

5.11.2.4   Calibration of the BETA 2000-type apparatus

- Put an empty cell in "Test" position on the apparatus.

- Open the helium-nitrogen mixture intake valve on the apparatus.

- Activate the apparatus, adjust the flow rate of the gaseous mixture to 15 mL/min under a pressure of 2×10^5 Pa.

- After a heating period on the order of 45 min, adjust the 0 of the apparatus by using the potentiometer provided.

- Adjust the "calibration" potentiometer to position 5.

The calibration will be done by injection of a determined volume (5 mL) of air; the air has the same thermal conductivity as the nitrogen.

60 sec after the injection, the air arrives in contact with the catharometers [sic].   An integrator calculates the area under the calibration peak.

After evaluation, a digital display indicates the surface area of the sample.

Note: It is possible to calibrate the apparatus using a product whose BET surface area has been determined by the gravimetric method.

5.11.2.5 Determination of the BET surface area

- Set the cell holder supporting the cell containing the degassed sample on the "Test" position of the measuring apparatus.
- Fill the Dewar vessel with liquid nitrogen.
- Put the apparatus on automatic cycle.
- Trigger the "Adsorb" key. The Dewar vessel rises immersing the cell in liquid nitrogen.
- The adsorption peak appears after 60 sec; the integrator automatically calculates the surface area of the sample and displays it. This value will not be taken into account.
- After the display, the Dewar vessel descends; the sample is heated and the adsorbed nitrogen is desorbed; the integrator calculates and displays the area under the desorption peak. It is this value that will be used.

The specific surface area, in meters squared per gram, is expressed by the formula:

$$S \text{ (BET) } m^2/g = \frac{S_1 \times 1 \times 100}{p \times (100 - H_{105})}$$

in which:

S_1 = area under the desorption peak in meters squared;

p = weight in grams of the sample placed in the bulb;

H_{105} = content in terms of volatile materials (5.2) in percentage of the product, measured by weight loss: 2 h at 105°C.

5.12 External specific surface area by CTAB (cetyltrimethylammonium bromide) adsorption (see paragraph 5.12.1)

Note: The contact surface between a reinforcing charge and an elastomer is a piece of basic data for the reinforcement. In effect, a charge can develop a porosity that cannot be accessed by the macromolecules[4]. It is therefore appropriate to differentiate the total surface area from the external surface area of the charge (for example, carbon black or precipitation silica).

It has been shown that the pores of a carbon black with diameter greater than 2 nm are accessible to the SBR elastomer with a molecular weight of 300,000.

Consequently, it is only on the external surface area of a reinforcing pigment that an elastomer can be attached, and therefore, this surface area is particularly significant with regard to the characteristics of the reinforcement.

Thus, with carbon blacks, a method for determining the external surface area by CTAB adsorption was proposed by J. Janzen and G. Krauss[5].

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[4]P. Aboytes, A. Voet - Rubber Chem. Technol. 43, 2 (1970) 464-469.

[5] J. Janzen, G. Krauss - Rubber Chem. Technol. 44 (1971) 1287, 1296.

This method cannot be applied directly to silica; in effect, the surface chemistry of silica is different from that of carbon blacks. The study of the adsorption of CTAB on silica in aqueous media shows that the adsorption must be performed at a pH of 9. Under these conditions, the apparent surface area of the CTAB molecule adsorbed on the silica is equal to 0.35 nm^2.

Knowing this surface area and the quantity of CTAB adsorbed, one can calculate the external specific surface area of the silica.

It can be shown that the CTAB specific surface area of the silica explains the dynamic properties and the tear strength of the vulcanization products[6,7].

5.12.1   Principle

This method relates to the measurement of the external specific surface area of silica, that is, of the specific surface area excluding the micropores. The external specific surface area of a silica is determined by the quantity of surfactant (CTAB) that the silica can adsorb. The surfactant used is hexadecyltrimethylammonium bromide, commonly designated by the initials CTAB.

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[6]A. Voet, J.C. Morawski, J.B. Donnet - Rubber Chem. Technol. 50, 2 (1977) 342-355.

[7]A. Voet, J.C. Morawski, J.B. Donnet - Reinforcement of elastomers by silica - Chapter 14 in "Elastomers": Criteria for engineering design C. Hepburn, R.W. Reynolds - Applied Science Publishers (1979).

Knowing the quantity of CTAB adsorbed for a given weight of silica and the space occupied by this molecule, one calculates the external specific surface area of the silica in meters squared per gram.

The quantity of CTAB adsorbed is determined by quantitative determination before and after adsorption using a solution of sodium di(2-ethylhexyl) sulfosuccinate (aerosol O T).

5.12.1.2 Method A

5.12.1.2.1 Reagents

During the test:

CTAB - 5.5 g/L solution

CTAB: Hexadecyltrimethylammonium bromide

$$CH_3-(CH_2)_{14}-CH_2-N^+(CH_3)_3Br^-$$

Weigh approximately 5.5 g of CTAB to the nearest 0.01 g, dissolve it in a 1-L volumetric flask with deionized or distilled water (heat very slightly, if necessary). The solution must be maintained in the absence of light at a temperature in the vicinity of 22°C, in order to avoid the beginning of crystallization.

This solution is used 12 days after its preparation, and is kept a maximum of two months after this period.

- Aerosol O T solution:

sodium di(2-ethylhexyl) sulfosuccinate.

This corresponds to the following formula:

$$\left[\begin{array}{l} \underset{O_3S}{\overset{\displaystyle CH_2}{\underset{\displaystyle}{\vert}}} \!\!\!\!\!\! \begin{array}{c} \\ \overset{\displaystyle}{\underset{\diagdown}{CH}} \end{array} \!\!\!\! \begin{array}{c} \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O - CH_2 - \overset{\displaystyle C_2H_5}{\overset{\displaystyle \vert}{CH}} - (CH_2)_3 - CH_3 \\ \\ \underset{\displaystyle C}{\overset{\displaystyle}{C}} - O - CH_2 - \underset{\displaystyle C_2H_5}{\overset{\displaystyle}{CH}} - (CH_2)_3 - CH_3 \\ \underset{\displaystyle O}{\overset{\displaystyle \|}{}} \end{array} \end{array} \right]^{-} \quad Na^+$$
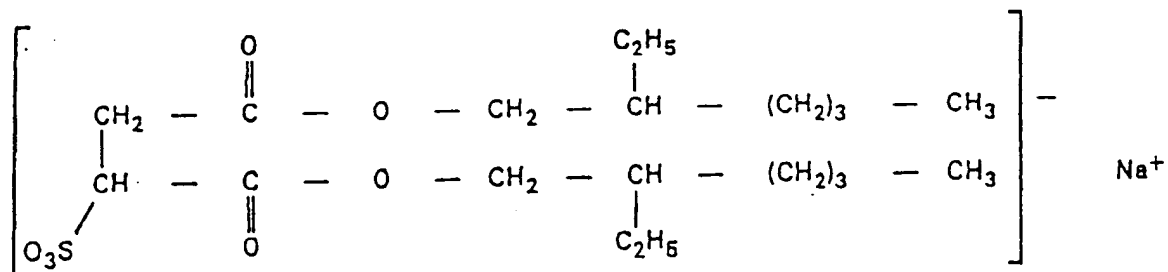
Weigh approximately 1.85 g of aerosol O T, dissolve it in a 1-L spherical flask with deionized (or distilled) water; heat slightly in order to accelerate dissolution, with magnetic stirring. This solution is used 12 days after its preparation, and is stored in the absence of light a maximum of two months after this period.

- deionized or distilled water,
- sodium hydroxide, titrated solution [NaOH] = 1 mol/L,
- chloroform,
- bromophenol blue, 0.02% solution.

5.12.1.2.2   Equipment
    - 1,000-mL volumetric flasks.
    - 100-mL volumetric flasks.
    - 10-, 50- and 100-mL pipettes with two lines.
    - 50- or 100-mL test tubes.
    - 250-mL conical flask.
    - 150- or 200-mL stoppered bottles.
    - Magnetic rods covered with polytetrafluoroethylene.

- Magnetic stirrer.
- 50-mL burette [calibrated] to the nearest 1/10 [mL]
- Balance accurate to the nearest 1/10 mg.
- pH meter.
- Glass electrode.
- Calomel reference electrode.
- Centrifuge.

5.12.1.2.3   Procedure

5.12.1.2.3.A   Quantitative determination of the CTAB solution using the solution of aerosol O T

- Fill a 50-mL burette with aerosol O T solution.
- Introduce into the 250-mL conical flask 10 mL of CTAB solution, using a pipette with two lines.
- Add 30 mL of chloroform.
- Add 50 mL of deionized or distilled water.
- Add 15 drops of 0.02% bromophenol.
- Add a drop of the sodium hydroxide solution (1 mol/L) in order to obtain a mauve coloring after the color change.
- Introduce a magnetic stirring bar and start the stirrer.

Introduce the aerosol O T solution into the conical flask, first rather rapidly and then drop by drop when approaching the color change. The mixture rapidly becomes milky blue.

With stirring stopped, the two phases are poorly distinguished. Continue the drop by drop introduction until the mixture becomes clearer.

When stirring is stopped one observes that the lower phase becomes blue and becomes clear. When the color change is near,

pour the aerosol O T solution 4 drops by 4 drops [sic]; possibly increase the speed of stirring in order to obtain better contact of the two phases. The end of the determination is marked by a change in coloring of the phases. In effect, almost at the end of the change, the lower organic phase becomes blue. At the end of the color change, the aqueous phase becomes mauve, and the organic phase colorless. Then, note V_1, the volume in milliliters of sodium di(2-ethylhexyl) sulfosuccinate, introduced.

5.12.1.2.3.B Adsorption of CTAB by the silica

To the nearest 1 mg, weigh approximately 500 mg of silica in the state it is in (not dried); introduce this quantity into a 150-mL bottle. Them introduce 100 mL of CTAB solution into this bottle using a pipette with 2 lines.

Introduce the magnetic stirring bar and stir gently for 15 min. After 15 min of stirring, adjust the pH of the suspension with the pH meter to between 9 and 9.5 using the sodium hydroxide solution. Continue stirring the solution in suspension for 1 h, verify the pH during this period of adsorption, and readjust it if necessary to between 9 and 9.5.

5.12.1.2.3.C Separation of the silica

The suspension obtained is centrifuged for 30 min.

Then, the aqueous phase is collected with the pipette, and it is introduced into a threaded bottle in order to determine the CTAB concentration.

5.12.1.2.3.D Quantitative determination of the CTAB after adsorption

Using a pipette, remove 10 mL of the CTAB solution obtained after adsorption and separation. Proceed with the determination as described in the preceding (5.12.1.2.3.B). During this determination, it is not necessary to add sodium hydroxide solution; let V_2 be the volume in milliliters of sodium di(2-ethylhexyl) sulfosuccinate used.

5.12.1.2.4   Expression of the results

Surface area occupied by a molecule of CTAB = 0.35 nm^2.

Relative molecular weight of CTAB = 366.44.

Surface area occupied by 1 g of CTAB = 578.435 m^2.

Weight of CTAB adsorbed by 0.500 g of silica:

$$(V_1 - V_2) \times \frac{10}{V_1} \times \frac{5.510^{-3}}{366.44} \times 366.44 \times 10$$

Weight of CTAB adsorbed per 1 g of silica:

$$\frac{V_1 - V_2}{V_1} \times 0.55 \times 2$$

CTAB surface area in m^2/g, of silica in its [original] state (not dried):

$$\frac{V_1 - V_2}{V_1} \times 0.55 \times 2 \times 578.435$$

CTAB surface are based on dried silica 2 h at 105°C:

CTAB surface area of silica in its [original] state x 100
100 - cotent of volatile materials as 105°C

5.12.1.3   Method B

5.12.1.3.1   Reagents

In the test:

All the chemical reagents used are of recognized analytical quality,

- deionized or distilled water,
- formaldehyde - 37% solution,
- CTAB (hexadecyltrimethylammonium bromide) - solution prepared in the following way: In a 2-L volumetric flask, dissolve 22 g of CTAB in 1.5 L of deionized (or distilled) water. After dissolution, adjust the volume to 2 L by addition of deionized (or distilled) water. Pour the contents of the volumetric flask into a stirred bottle with a volume of 5 L. Again fill the flask with 2 L of deionized (or distilled) water, adjusting it to the graduation line; stopper the flask and homogenize manually in order to incorporate the fraction of residual solution that is attached to the walls; then pour the contents into the 5 L bottle.

- sodium di(2-ethylhexyl) sulfosuccinate: solution of aerosol O T prepared in the following way: In a 2-L volumetric flask, dissolve 6.924 g of aerosol O T in 1.5 L of deionized (or distilled) water with addition of 10 mL of 37% formaldehyde solution. After dissolution, fill to 2 L with deionized (or

distilled) water. Pour the contents of the volumetric flask into a stirred 5-L bottle. Fill the 2-L flask again with deionized (or distilled) water, adjusting it to the graduation line; stopper the flask, homogenize manually in order to collect the fractions of product remaining attached to the walls, then pour the contents into the 5-L bottle.

This solution is used 12 days after its preparation and is kept in the absence of light for a maximum of two months after this period.

5.12.1.3.2   Equipment

Two 2-L volumetric flasks,

Two 5-L volumetric flasks,

Eight tared 80-mL bottles,

1 precision balance accurate to the nearest 1/10 mg,

1 oven regulated to 105°C $\pm$ 2°C

1 desiccator containing silica gel,

One 50-mL burette [accurate] to the nearest 0.001%,

1 burette with electrode for measuring pH,

8 magnetic stirrers turning at a speed of 2,000 rpm (maximum speed),

8 magnetic stirring bars caoted with polytetrafluoroethylene, length 20 mm,

1 high-speed thermoregulated centrifuge (acceleration 100,000 m·sec^{-2}),

1 automatic micropipette,

1 quantitative determination line [sic; apparatus] including:

● 1 titriprocessor [sic; possibly, automatic titrator],

  1 automatic burette,

●. 1 spectrometer used in turbidity,

● 250-mL beakers (covered with aluminum foil in order to
protect the determination from stray light).

5.12.1.3.3   Procedure

a) Preparation of the samples

    − Modulation of the test samples as a function of the
external specific surface area of the silica:

Estimated external specific surface area m^2/g	Test samples g
90	0,500
120	0,375
176	0,260
220	0,200
300	0,150

    Preliminary drying of the silica:

    − in a tared bottle (5.12.1.3.2) dried for 1 h in the oven
at 105°C ± 2°C, introduce a weight of silica x according to the
preceding table,

    − after drying in the oven at 105°C ± 2°C for 2 h, remove
the tared bottle from the oven, stopper it immediately, and allow
to cool for 2 h.

Another weighing operation gives the weight m of the dried silica sample whose external surface area will be measured.

Adsorption of the CTAB solution by the silica
- Adjusting to pH = 9:
    • Using an automatic burette, pour 100 mL of 5.5 g/L CTAB solution on the silica.

    • Stir the suspension obtained with the magnetic stirrer for 30 min.

    • Stop the stirring, measure the pH.

    • Bring the pH to 9 with 0.1 mol/L soda, using the burette, stir again for 1 h, verify that the pH is equal to 9, readjust it if necessary, and maintain stirring for another hour.

    • Note the quantity of 0.1 mol/L soda added, volume V_3, in milliliters.

- Centrifugation:
    After slight settling of the suspension obtained, centrifuge the supernatant at 100,000 m·sec^2 verifying that the temperature does not exceed 30°C. The duration of centrifugation is 30 min.

- Quantitative determination of the CTAB after adsorption:
    Determination using the aerosol O T solution with burette coupled with a titriprocessor. Detection of the maximum turbidity by spectrophotometer.

- Reference determination:

  • Remove 5 mL of the 5.5 g/L CTAB solution (5.12.1.3.1) using the micropipette, and introduce this quantity into a 250-mL beaker.

  • Add 200 mL of deionized (or distilled) water.

  • Put in the absence of light by surrounding the beaker with aluminum foil.

  • Adjust the transmittance to 100% on the spectrometer.

  • Adjust the stirring speed to 400 rpm (magnetic stirring bar, length 20 mm).

  • Start the determination using the titriprocessor.

  • The aerosol O T solution is introduced rapidly until 95% transmittance; then the speed of introduction is controlled so as to arrive slowly at the equivalence point, which should correspond to a detected voltage between 400 and 600 mV, which is a sign of correct dilution of the solution to be analyzed.

  The volume of the aerosol O T solution is V_1, in milliliters.

- Determination of the CTAB supernatant after adsorption:

  • Remove 5 mL of the supernatant using the pipette,

  • Dilute with 200 mL of deionized (or distilled) water,

  • Determine the CTAB using aerosol O T in the same manner as for the reference determination.

  The volume of aerosol O T introduced for the equivalence point is V_2.

5.12.1.3.4   Expression of the results

Surface area occupied by one molecule of CTAB = 0.35 nm^2.

Relative molecular weight of CTAB = 366.44.

Surface area occupied by 1 g of CTAB

$$\frac{35.10^{-20} \times 6,02.10^{23}}{366,44} = 578,435 \text{ m}^2$$

The external specific surface area of the silica dried for 2 h at 105°C $\pm$ 2°C (paragraph 5.2) is equal to:

$$\frac{V_1 - V'_2}{V_1} \times \frac{0,55 \times 578,435}{m}$$

in which:

$$V'_2 = \frac{V_2 \times (100 + V_3)}{100}$$

V_1 = volume of aerosol in milliliters, introduced for the determination of the reference;

V_2 = volume of aerosol in milliliters, introduced for the determination of the solution of supernatant;

V_3 = volume in milliliters of sodium hydroxide (0.1 mol/L) introduced to adjust the pH to 9;

m = weight in grams of the sample of dried silica.

5.13 Tests on mixtures

5.13.1   Constitution of the mixture expressed in grams

Butadiene-styrene copolymer (type 1500)	100
Silica	40
Zinc oxide NF T 45-002	3
Stearic acid NF T 45-004	1.5
Bis(dimethylthiocarbamyl) disulfide	2.0
N-tert-Butyl-2-benzothiazolesulfenamide	2.0
Sulfur NF T 45-003	0.4
Total	148.9

Note: This formula can be modified as a function of the classes of specific surface areas, particularly for the high specific surface areas. This modification will be done in a manner agreed upon by the contracting parties.

5.13.2   Procedure

5.13.2.1 Equipment and procedure
    The equipment and the procedure, the mixing, and the vulcanization must be in accordance with NF T 43-006.

5.13.2.2 Mixing with an open mixing mill
    The weight in grams of mixture used in a standardized open mixing mill must be equal to four times the weight of the test formula. The surface temperature of the cylinders must be maintained at 30°C ± 5°C during the whole mixing operation. The

weight of the mixture obtained must not differ by more than 2.0% from the total weight of the ingredients.

Duration (min)

- With the separation between the cylinders adjusted to 1.0 mm, form the rubber sleeve, then cut the sleeve to 3/4 of its width every 30 sec, on each side alternately: 2
- Add the sulfur slowly and regularly along the rim. When the sulfur has been incorporated, cut the sleeve to 3/4 on each side: 2
- Add approximately 10% silica and zinc oxide. No cut should be made at this stage. 4
- Again add 10% silica and stearic acid, without cutting the mixture. 4
- Add the rest of the silica slowly. Adjust the separation so that the rim has a diameter of approximately 15 mm. Do not cut the mixture during the incorporation of the silica. Add the products that fell in the tank, and when any silica is incorporated, cut the mixture once on each side. . . 10
- Add the accelerator, and cut the mixture to 3/4 of the sleeve three times on each side. 4
- Cut the sleeve and remove it from the mixer. Adjust the separation of the cylinders to 0.8 mm and allow the mixture to pass three times between the cylinders, forming a roll and introducing it by one of its ends. 2
- Allow the mixture to turn for 5 min through the mixer, with a suitable spacing of the cylinders so that the rim has a diameter of approximately 15 mm. 5

- Draw the mixture into a sheet with a thickness of approximately 5 mm, and check its weight.

Total duration 33

- Condition the mixture for between 2 and 24 h.

- If further mixing is necessary, this must be done in accordance with the following procedure:

With the surface temperature of the cylinders maintained at 30°C ± 5°C, adjust the separation of the cylinders to 0.2 mm and weigh the mixture once (without forming a sleeve) between the cylinders.

Adjust the separation of the cylinders to approximately 3 mm. Form the rubber sleeve and allow the mixture to turn, with a rather large rim, for 5 min without cutting.

Increase the separation of the cylinders so as to obtain a minimum thickness of the sheet of 6 mm and pass the mixture between the cylinders four times, folding it over itself each time.

Remove the necessary samples for the determination of the vulcanization characteristics.

Draw the mixture into a sheet, taking care to adjust the separation of the cylinders so as to obtain a final thickness of approximately 2.2 mm for the preparation of test pieces in a dumbbell shape (or another thickness appropriate for the preparation of test pieces in rings).

Vulcanize the test plates as soon as possible.

5.13.2.3 Vulcanization

Vulcanize the test plates at 150°C for 15 min. Condition the vulcanized plates for between 16 and 72 h.

5.13.2.4 Tests on unvulcanized mixtures

Determine the consistency using a shear viscometer, according to standard NF T 43-005.

5.13.2.5 Evaluation of the vulcanization characteristics

Determine the tensile-elongation properties (tensile stress at 500% elongation, tensile strength and elongation at break) according to standard NF T 46-002.

Determine the hardness according to standard NF T 46-003. Determine the tear strength according to standard NF T 46-007.

6   TEST REPORT

The report must refer to the present standard, and besides the results obtained, it must mention the incidents of operation not foreseen in the standard and capable of having influenced the results.

7   BIBLIOGRAPHY

NF X 02-206   Magnitudes, units, and symbols of electricity and magnetism.

ISO 31/0   General principles concerning magnitudes, units and symbols.

ISO 787/2 General methods for testing pigments and load materials – Part 2: Determination of volatile materials at 105°C.

ISO 3262   Fillers for paints.

Appendix A

(not an integral part of the standard)

This program is written in Basic for an HP 85 calculator. There is a standard NF Z 65-600 "Minimal Basic programming languages" This program differs from it particularly in the "systems" commands.

```
10  ! ***********************
20  !      Programme "BET" (1)
30  !
40  ! Recherche du Domaine BET (2)
50  !   Trace de la droite BET .
60  ! ***********************
70  OPTION BASE 1
80  DIM E$[10],F$[32],N$[6]
90  DIM C(10),P2(50),W(50),A1(50
    ),A2(50),T(20)        (3)
100 CLEAR
110 DISP "NOM DU FICHIER" @ INPU
    T N$
120 ASSIGN# 3 TO N$
130 READ# 3 ; E$,F$,N$,M,N4
140 READ# 3,2
150 J=0
160 FOR I=1 TO N4
170 READ# 3 ; P2(I),W(I)
180 IF P2(I)<.04 THEN GOTO 220
190 IF P2(I)>.4 THEN N4=J @ GOTO
    280
200 J=J+1
210 A1(J)=P2(I) @ A2(J)=P2(I)/(W
    (I)*(1-P2(I)))
220 NEXT I
230 ! -----------------------
240 !    ANALYSE DE VARIANCE
250 !
260 !         DEGRE 1      (4)
270 ! -----------------------
280 T1=1
290 DISP @ DISP USING 300 ; N4
300 IMAGE "CALCUL EN COURS AVEC (5)
    ",2D," POINTS"
310 Y(1)=INF @ Y(2)=-INF
320 FOR I=1 TO 10 @ C(I)=0 @ NEX
    T I
330 FOR I=2 TO 7 @ E(I)=0 @ NEXT
    I
340 E(1)=1
350 FOR I1=1 TO N4
360 E(2)=A1(I1)
370 E(3)=A1(I1)*A1(I1)
380 E(4)=A2(I1)
390 A=0
400 FOR I=1 TO 4
410 FOR J=I TO 4
420 A=A+1
430 C(A)=C(A)+E(I)*E(J)
440 NEXT J
450 NEXT I
460 IF Y(2)<A1(I1) THEN Y(2)=A1(
    I1) @ Y(4)=A2(I1)
470 IF Y(1)>A1(I1) THEN Y(1)=A1(
    I1) @ Y(3)=A2(I1)
480 NEXT I1
490 M1=C(3)-C(2)^2/N4
500 M2=C(10)-C(4)^2/N4
510 M3=C(7)-C(2)*C(4)/N4
```

Appendix A (continued)

```
520 K2=M3/M1 ! PENTE DE LA DROIT⑥
    E
530 K1=(C(4)-K2*C(2))/N4 ! ORDON ⑦
    NEE A L'ORIGINE
540 M4=(M2-K2^2*M1)/(N4-2)
550 K3=SQR(M4/M1) ! ECART-TYPE S⑧
    UR K2
560 K0=SQR(M4/N4*(C(2)^2/N4/M1+1 ⑨
    )) ! ECART-TYPE SUR K1
570 ! ----------------------
580 !          DEGRE 2      ⑩
590 ! ----------------------
600 P=1
610 FOR J=1 TO 3
620 C(P)=SQR(C(P))
630 FOR I=1 TO 4-J
640 C(P+I)=C(P+I)/C(P)
650 NEXT I
660 S,R=P+I
670 FOR L=1 TO 3-J
680 P=P+1
690 FOR M=1 TO 5-J-L
700 C(R+M-1)=C(M+R-1)-C(P)*C(P+M
    -1)
710 NEXT M
720 R=R+M-1
730 NEXT L
740 P=S
750 NEXT J
760 T=9
770 FOR I=1 TO 2
780 T=T-I
790 C(T)=1/C(T)
800 FOR J=1 TO 3-I
810 P=4-I-J
820 P=P*(4-(P-1)/2)-I
830 R=P-J @ S=0 @ Z=I+J+1
840 V=P
850 FOR M=1 TO J
860 V=V+Z-M
870 S=S-C(R+M)*C(V)
880 NEXT M
890 C(P)=S/C(R)
900 NEXT J
910 NEXT I
920 F=C(9)*C(9)*(N4-3)/(C(10)-C(
    4)^2-C(7)^2-C(9)^2)
930 DISP USING "4A,3D.2D" ; "F
    =",F
940 IF T1=1 THEN GOSUB 1530
950 F0=T(N4-3)^2
960 DISP USING "4A,3D.2D" ; "Fo
    =",F0
970 IF N4>5 THEN T5=0 @ GOTO 100
    0
980 DISP @ DISP "SORTIE A 5 POIN⑪
    TS"
990 T5=1 @ GOTO 1050
1000 IF F>F0 THEN GOTO 1320
1010 ! ----------------------
```

Appendix A (continued)

```
1020 ! INTERVALLES DE CONFIANCE  ⑫
1030 ! ------------------------
1040 T3=0
1050 IF K1<0 THEN E1=1/K2 @ T3=1
     @ GOTO 1140
1060 T0=T(N4-2)
1070 E1=1/(K1+K2)
1080 E3=1/(K1+K2+T0*K0+T0*K3)
1090 E2=1/(K1+K2-T0*K0-T0*K3)
1100 E4=1+K2/K1
1110 E5=1+(K2+T0*K3)/(K1-T0*K0)
1120 E6=1+(K2-T0*K3)/(K1+T0*K0)
1130 P1=(SQR(E4)-1)/(E4-1)
1140 IF E1<Y(1)/Y(3)/(1-Y(1)) TH
     EN GOTO 1170
1150 IF E1>Y(2)/Y(4)/(1-Y(2)) TH
     EN GOTO 1170
1160 GOTO 1180
1170 DISP "   Vm N'EST PAS DANS  ⑬
     LE DOMAINE LINEAIRE" @ T3=1
1180 DISP USING "4A,3D.D,5A" ; "
     S = ",4.35*E1," m2/g"
1190 DISP USING "4A,3D" ; "C = "
     ,E4
1200 DISP @ DISP "LA MONOCOUCHE  ⑭
     EST ATTEINTE POUR"
1210 DISP USING 1220 ; P1
1220 IMAGE "           P/Po = ",Z.
     3D
1230 DISP @ DISP USING 1240 ; Y(
     1),Y(2)
1240 IMAGE "Domaine Lineaire :",  ⑮
     Z.3D," - ",Z.3D
1250 GOSUB 1660
1260 ASSIGN# 1 TO N$
1270 READ# 1,1 ; E$,F$,N$,M,N1,H
     2
1280 PRINT# 1,1 ; E$,F$,N$,M,N1,
     H2,E1
1290 ASSIGN# 1 TO *
1300 DISP @ DISP @ DISP "
           FIN"
1310 END
1320 ! ------------------------
1330 ! ELIMINATION D'UN POINT  ⑯
1340 ! ------------------------
1350 Y1=EPS
1360 FOR I=1 TO N4
1370 Y=K1+K2*A1(I)
1380 IF ABS(A2(I)-Y)>Y1 THEN N8=
     I @ Y1=ABS(A2(I)-Y)
1390 NEXT I
1400 DISP "J'elimine le ";N8;"em  ⑰
     e point"
1410 DISP USING 1420 ; A1(N8)
1420 IMAGE "situe a P/Po =",D.3D  ⑱
1430 FOR I=N8 TO N4-1
1440 A1(I)=A1(I+1)
1450 A2(I)=A2(I+1)
1460 NEXT I
```

Appendix A (continued)

```
1470 N4=N4-1
1480 GOTO 290
1490 ! -------------------------
1500 !   TABLE DES t DE STUDENT (19)
1510 !     A 95 %  BILATERAL
1520 ! -------------------------
1530 T(2)=4.303 @ T(3)=3.182
1540 T(4)=2.776 @ T(5)=2.571
1550 T(6)=2.447 @ T(7)=2.365
1560 T(8)=2.306 @ T(9)=2.262
1570 T(10)=2.228 @ T(11)=2.201
1580 T(12)=2.179 @ T(13)=2.16
1590 T(14)=2.145 @ T(15)=2.131
1600 T(16)=2.12 @ T(17)=2.11
1610 T(18)=2.101 @ T(19)=2.093
1620 T1=2 @ RETURN
1630 ! -------------------------
1640 !    TRACE DE LA DROITE    (20)
1650 ! -------------------------
1660 DISP @ DISP
1670 DISP " EDITION SUR LA TABLE (21)
     TRACANTE"
1680 DISP "         APPUYEZ SUR CONT(22)
     " @ PAUSE
1690 PRINTER IS 705,50
1700 PRINT "IH"
1710 PLOTTER IS 705
1720 LIMIT 0,250,0,180
1730 IF A2(N4)<.0001 THEN A=INT(
     A2(N4)*100000+1)/100000 @ G
     OTO 1790
1740 IF A2(N4)<.001 THEN A=INT(A
     2(N4)*10000+1)/10000 @ GOTO
      1790
1750 IF A2(N4)<.01 THEN A=INT(A2
     (N4)*100+1)/100 @ GOTO 1790
1760 IF A2(N4)<.1 THEN A=INT(A2(
     N4)*100+1)/100 @ GOTO 1790
1770 IF A2(N4)<1 THEN A=INT(A2(N
     4)/10+1)/10 @ GOTO 1790
1780 IF A2(N4)>1 THEN A=INT(A2(N
     4))+1
1790 FRAME
1800 LOCATE 15,85,15,95
1810 SCALE 0,.4,0,A
1820 FXD 2,3
1830 LAXES -.02,A/10,0,0,5,2
1840 MOVE 0,K1
1850 DRAW .4,K1+.4*K2
1860 MOVE 0,0
1870 PRINT "SM+"
1880 FOR I=1 TO N4
1890 PENUP
1900 PLOT A1(I),A2(I)
1910 NEXT I
1920 PRINT "SM"
1930 MOVE .2,-(A/8)
1940 LORG 4 @ CSIZE 3,.5,10
1950 LABEL "Pression Relative" (23)
1960 MOVE .2,A*1.02
```

Appendix A (continued)

```
1970 CSIZE 5,.5,0
1980 LABEL "DROITE B.E.T."  (24)
1990 MOVE -.06,A/2
2000 DEG @ LDIR 90 @ CSIZE 3,.5,
     10
2010 LABEL "P/V(Po-P)"
2020 SETGU @ LDIR 0
2030 MOVE 95,84
2040 LORG 1 @ CSIZE 4,.4,0
2050 LABEL F$
2060 MOVE 95,88
2070 CSIZE 3,.5,10
2080 LABEL "Echantillon:"  (25)
2090 MOVE 95,80 @ LORG 1 @ CSIZE
     3,.5,0
2100 LABEL "Le ";E$;"      essai: (26)
     ";N$
2110 MOVE 139,78
2120 DRAW 90,78
2130 MOVE 139,91
2140 DRAW 90,91
2150 MOVE 90,100 @ DRAW 90,0
2160 MOVE 95,72
2170 CSIZE 3,.5,0
2180 LABEL "VOLUME MONOMOLECULAI (27)
     RE :"
2190 MOVE 100,68
2200 IF T3=1 THEN LABEL USING "8 (28)
     A,3D.D,6A" ; "ENVIRON",E1,"
     cm3/9" @ GOTO 2240
2210 LABEL USING "4A,3D.D,6A" ;
     "Vm =",E1," cm3/9"
2220 MOVE 95,64
2230 LABEL USING "13A,3D.D,3A,3D (29)
     .D" ; "Compris entre",E3,"
     et",E2
2240 MOVE 95,58
2250 LABEL "CONSTANTE C :" (30)
2260 MOVE 100,54
2270 IF T3=1 THEN LABEL USING "8
     A,5D" ; "ENVIRON",E4 @ GOTO
     2310            (31)
2280 LABEL USING "3A,5D" ; "C ="
     ,E4
2290 MOVE 95,50
2300 LABEL USING "13A,5D,3A,5D"
     ; "Compris entre",E6," et", (32)
     E5
2310 MOVE 95,48
2320 LABEL "SURFACE SPECIFIQUE :(33)
     "
2330 MOVE 100,36
2340 IF T3=1 THEN LABEL USING "8 (34)
     A,4D.D,5A" ; "ENVIRON",E1*4
     .35," m2/9" @ GOTO 2410
2350 LABEL USING "3A,4D.D,5A" ;
     "S =",E1*4.35," m2/9"
2360 MOVE 95,32
2370 LABEL USING "13A,4D.D,3A,4D
     .D" ; "Compris entre",E3*4. (35)
     35," et",E2*4.35
```

Appendix A (continued)

```
2380 IF T5=0 THEN GOTO 2410
2390 MOVE 100,20
2400 LABEL "SORTIE A 5 POINTS"        36
2410 MOVE 95,15
2420 LABEL USING "16A,2D.2D" ; "DSDR/CM =          ",F
2430 MOVE 95,10
2440 LABEL USING "16A,2D.2D" ; "F de Snedecor = ",FO
2450 RETURN                                    37
```

```
Key: 1    "BET" Program
     2    Search for the BET domain
          Plotting of the BET line
     3    Filename
     4    Analysis of variance
          First-order
     5    Calculation in progress with 2D points
     6    Slope of the line
     7    Ordinate at the origin
     8    Standard deviation on K2
     9    Standard deviation on K1
    10    Second-order
    11    Output with 5 points
    12    Confidence intervals
    13    Vm is not in the linear domain
    14    Monolayer is reached for
    15    Linear domain
    16    Elimination of a point
    17    I eliminated the N8th point
    18    Located at P/Po =
    19    Table of Student's t, 95%, two-tailed
    20    Plotting of the line
    21    Printing on the plotting table
    22    Press cont
    23    Relative pressure
    24    BET line
    25    Sample
    26    The E$ test:
    27    Monomolecular volume
    28    Approximately
    29    Between E3 and E2
    30    Constant C
    31    Approximately
    32    Between E6 and E5
    33    Specific surface area
    34    Approximately
    35    Between E3*4.35 and E2*4.35
    36    Output with 5 points
    37    Snedecor F =
```

Appendix B

(not an integral part of the standard)
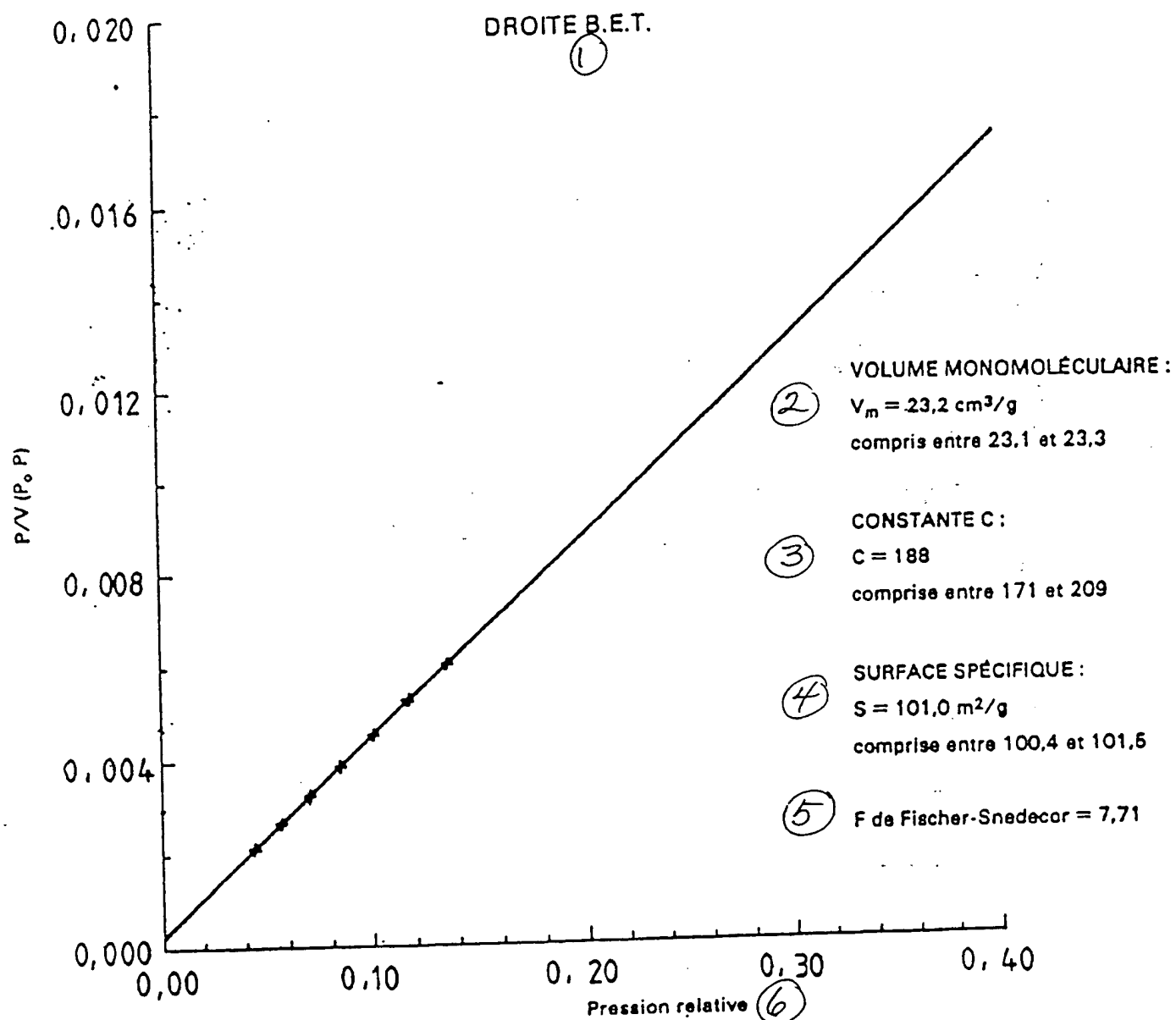
Key: 1   BET line
      2   Monomolecular volume:
          $V_m = 23.2$ cm^3/g
          between 23.1 and 23.3
      3   Constant C:
          C = 188
          between 171 and 209
      4   Specific surface area:
          S = 101.0 m^2/g
          between 100.4 and 101.5
      5   Fischer-Snedecor F = 7.71
      6   Relative pressure